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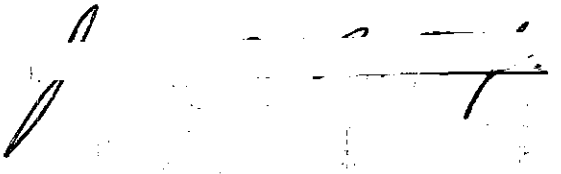

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NEW MASKING APPLICATIONS FOR CHELOMETRIC TITRATIONS AND PHOTOMETRIC DETERMINATIONS

A THESIS

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by

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NEW MASKING APPLICATIONS FOR CHELOMETRIC TITRATIONS AND PHOTOMETRIC DETERMINATIONS

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SUMMARY

Selectivity in an analytical procedure is most often achieved by controlling certain important factors. In general, these factors are the nature of the reagent used, the pH of the solution, and the presence of masking reagents. Of these factors, the presence of masking reagents is the most important. In the present study, "low stability masking" (i.e., masking by the formation of relatively weak complexes), "partial masking" (i.e., masking by the addition of a fraction of the amount of a masking reagent equivalent to the species to be masked), and the photometric method of end point detection have been investigated. "Low stability masking" has been applied to the iron-bismuth and the gallium-indium systems. "Partial masking" has been applied to the cobalt-nickel system. The following methods have been developed: a photometric titration of small amounts of iron in the presence of bismuth, a selective titration to a visual end point of small amounts of gallium in the presence of indium, and a photometric determination of traces of cobalt in the presence of nickel.

Due to certain deviations from linearity observed for the phototitrator used for part of this work, a study of the cause of these deviations was undertaken. This study included the designing and testing of a new phototitrator circuit. Also, a comparison of the quality of the end points obtained using both the photometric and the potentiometric methods of end point detection was made.

Photometric Titration of Iron in the Presence of Bismuth

Iron(III) can be titrated in the presence of large amounts of bismuth and some other metals in the following manner. Ammonium chloride is added to the sample until a saturated solution is obtained. The pH is adjusted to between 2-3, and sulfosalicylic acid is added as indicator. The titration is performed photometrically at about 508 mμ with (ethylenedinitrilo)tetraacetic acid (EDTA) as titrant. Correct results have been obtained with bismuth:iron molar ratios up to 3000:1. Interferences by some other metal ions have been investigated.

Titration of Gallium in the Presence of Indium

Gallium can be titrated to a visual end point with EDTA at pH 1.3-1.4 by using Xylenol Orange as indicator. Indium can be masked by chloride; a concentration of 25 g of ammonium chloride per 100 ml is necessary. Correct results and good end points are obtained with indium:gallium molar ratios up to 300:1. Interferences by some other metal ions have been investigated.

Photometric Determination of Traces of Cobalt in Nickel

Cobalt can be determined photometrically as the green Co(III)-PAN complex in the following manner. About 98 percent of the amount of EDTA equivalent to the nickel present in the sample is added. Ethanol is added until a 50 percent ethanol-water solution is obtained, and the pH is adjusted to 2.0-2.5. PAN indicator is added, and the solution is aerated for one hour or more. The Co(III)-PAN complex and the excess PAN are extracted into chloroform, and the absorbance of the extract at 625 mμ is measured. Correct results have been obtained for nickel:cobalt molar

ratios up to 20,000:1. Interferences by some other metals have been investigated.

Linearity Studies

Deviations from linearity at wavelengths between 400-500 mμ were observed for both the original model of the phototitrator used in this work and a modified version employing a different photodetector and circuit. Investigations have been made which show that these deviations are due to nonmonochromacy of the light striking the photodetector.

Photometric and Potentiometric End Point Studies

Simultaneous photometric and potentiometric titrations of copper(II) with EDTA at several different pH values have been performed. The resultant titration curves have been compared to theoretically calculated titration curves, and the difference in the quality and utility of the end points obtained by both methods has been pointed out.

CHAPTER I

INTRODUCTION

Definitions

In the introduction of a topic such as the one which follows, it is helpful to preface any discussion with a few definitions. These definitions may differ slightly in denotation from those found in other literature, but they will be applied uniformly throughout this discussion.

A metal complex is a species formed by the coordinative attachment of one or more molecules or ions to a metal ion in solution. The species coordinated about the metal ion are called ligands. Ligands which are capable of occupying only one coordinating position on a metal ion are said to be unidentate. Ligands which are capable of forming two, three, etc. bonds to metal ions are said to be bidentate; tridentate; etc. In general, a polydentate ligand is one which is capable of occupying several coordination positions on metal ions simultaneously. The term chelate complex, introduced by Morgan and Drew (1) denoted a particular type of complex formed by a polydentate ligand. A chelate complex is one in which the metal ion is a member of one or more rings; these rings are usually five- or six-membered in the analytically important complexes. The word chelon is the name for a special class of chelating agents, the polyaminocarboxylic acids, which form stable, water soluble and predominately 1:1, complexes with metal ions. A complexometric titration is any titration which is based on a complexation reaction. Complexometric titrations in

which the resulting complex species is a chelate are called chelatometric titrations. Chelatometric titrations based on the use of chelons are called chelometric titrations. Although most of the methods reported in the literature to date have been chelometric methods, often no distinction is drawn between complexometric, chelatometric, and chelometric titrations.

Historical Review

Until 1945-6 when Schwarzenbach introduced (ethylenedinitrilo)tetraacetic acid (EDTA) as a titrant for metal ions (2, 3, 4), there were few methods which involved complexation as a basis for a titration. The first application of a complexation reaction to titrimetry was reported by Marozeau in 1832 (5). In this procedure, iodide is titrated with mercury(II) to form the complex HgI^{-2}_4; the end point is indicated by the precipitation of HgI_2 according to

$$Hg^{+2} + HgI^{-2}_4 = 2HgI_2$$

Only a limited number of titrations of this type have been developed, the best known of which are the titration of cyanide with silver (6), chloride with mercury (7), and nickel or copper with cyanide (8,9).

After EDTA was introduced it found applications for the determination of nearly all polyvalent metal ions. EDTA forms stable 1:1 complexes with most metal ions. Chelometric titrations involving EDTA and related compounds have become increasingly important, and the literature in the field already numbers several thousand publications. Schwarzenbach and Flaschka (10) have recently reviewed the scope and theoretical aspects of

chelometric titrations as well as the practical applications.

The Stability Constant

The equilibria of complex compounds in solution can be defined by equations based on the law of mass action. The formulation of this law states that for a complexation reaction

$$mM + nL = M_mL_n$$

the concentrations of the components in solution are related by the equation

$$K_{M_mL_n} = \frac{[M_mL_n]}{[M]^m[L]^n}$$

where the brackets denote concentrations and $K_{M_mL_n}$ is the stability constant for the complexation reaction. For our purposes only mononuclear complexes (i.e., m = 1) will be considered. In this case the addition of ligands to the central metal ion will take place in a stepwise manner as given by the expressions

$$M + L = ML$$

$$ML + L = ML_2$$

$$\vdots$$

$$ML_{n-1} + L = ML_n$$

The equilibrium constant for each complexation step is then

$$k_1 = \frac{[ML]}{[M][L]}$$

$$k_2 = \frac{[ML_2]}{[ML][L]}$$

$$k_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

These constants are called the consecutive or stepwise stability constants. The overall complexation reaction may be written as

$$M + nL = ML_n$$

It can be easily shown that K_{ML_n} is the product of the stepwise stability constants for the complexation reaction. That is

$$K_{ML_n} = k_1 \, k_2 \ldots . k_n$$

This constant is known as the overall stability constant or the stability product.

If the brackets in the expression for the stability constants given above represent the activities of the enclosed species, the particular stability constant is called the thermodynamic stability constant. This constant, however, is of little practical value for the purposes of analytical chemistry and is mostly of interest to physical chemists. It is more practical to let the brackets represent the molar concentration of the species involved. In fact, the stability constants of most complex

compounds are usually determined as concentration constants at a given ionic strength. Ringbom (11) has shown that the effect of changes of ionic strength, μ, on concentration constants can usually be neglected in the range between $\mu = 0.1$ to 0.5. Fortunately this is the range in which chelometric titrations are commonly performed.

The complexation reaction between a metal, M, and a chelon, Y, may be written as

$$M + Y = MY$$

the equilibrium constant is then

$$K_{MY} = \frac{[MY]}{[M][Y]}$$

The expression for the stability constant in terms of molar concentration as written above is called the absolute stability constant, K_{abs}. In the absolute stability constant, only the concentrations of the "free" metal ion (i.e., metal ion which is present as the aquo complex), the fully dissociated Y, and the complex MY are used. The applicability of the absolute stability constant to practical calculations is complicated by the fact that the many possible side reactions of the chelon and metal can affect these concentrations. For example, reactions of the metal with other complex formers in the solution, protonation of the chelon, and the formation of protonated and mixed complexes of the type M(HY), M(OH)Y, and MZY must often be taken into consideration.

In order to take the various side reactions into account in a cal-

culation, an expansion of the approach is necessary. Such an expansion was introduced by Schwarzenbach (12) and later extended by Ringbom (11) and involves the concepts of the conditional stability constant. The conditional stability constant is written as a function of the total concentration of the complex MY and of the metal and chelon which have not participated in the complex formation. It compensates for the effects of any competing side reactions and is related to the absolute stability constant by easily calculated factors. When conditional stability constants are used, all titration calculations can be made as if only the primary reaction were taking place.

Since, in the determination of stability constants, some concentrations are measured potentiometrically, another type of stability constant, usually a mixed constant, is in practical usage. A mixed constant involves both activities and concentrations in the stability constant expression. Thus if concentration constants are to be used in a calculation, all potentiometrically determined quantities (usually pH) must be corrected, since these quantities are activities rather than concentrations. This correction can be easily avoided by the use of mixed stability constants. Thus the equilibrium expression for a mixed stability constant contains hydrogen and hydroxide ion activities, but contains concentrations of all other species. Both absolute and conditional stability constants can be expressed as mixed constants when hydrogen or hydroxide ions participate in the equilibrium.

The Concept of Conditional Stability Constants

The expression for a conditional stability constant for a complexa-

tion reaction can be derived from the absolute stability constant by consideration of a factor calculated for each side reaction. The calculation of these factors will be treated separately in the following sections.

The Influence of pH, the α Factor

EDTA and related compounds are polyprotic acids and are present as completely dissociated anions only in strongly alkaline solutions. At a pH lower than about 10-11, the uncomplexed chelon will be present in its various protonated forms, HY^{-3}, H_2Y^{-2}, H_3Y^{-1}, and H_4Y. The relative amounts of these protonated forms will vary with the pH and the acid dissociation constants of the particular chelon. Hydrogen ion is, in effect, competing with the metal ion for the chelon, and thus the apparent stability of the metal complex is reduced at a lower pH. In order to account for this effect, the stability constant under the actual solution conditions must be calculated. The resulting constant is called the conditional (sometimes the apparent or effective) stability constant. A factor, α_H, can be used to calculate the conditional stability constant from the absolute stability constant. The subscript H specifies that the hydrogen ion concentration dependence is being considered.

In the following discussions, all calculations will be made on the basis of molar concentrations, as symbolized by brackets, with the exception that hydrogen ion activity, denoted by parentheses, will be employed. Here, and throughout this discussion, charges are omitted whenever they are not required for clarity.

If protonation of the ligand is the only side reaction, the conditional stability constant at any pH may be expressed as

$$K_{cond} = \frac{[MY]}{[M][Y]^*} \tag{1}$$

where $[Y]^*$ denotes the total concentration of chelon not combined with the metal ion, which includes the completely dissociated and all the protonated forms which may exist at a particular pH. Only a fraction of the chelon not combined with the metal ion, $[Y]^*$, is present in its fully dissociated form.

The quantity $[Y]^*$ is related to the molar concentration of the completely dissociated chelon $[Y]$ by the relation

$$[Y]^* = [Y]\alpha_H \tag{2}$$

Assuming that Y is a tetraprotic acid such as EDTA, the material balance gives

$$[Y]^* = [Y] + [HY] + [H_2Y] + [H_3Y] + [H_4Y] \tag{3}$$

In order to express equation (3) in a form which shows the relationship between $[Y]^*$ and hydrogen ion concentration, expressions for the various terms in the equation are obtained by introducing the stepwise acid dissociation constants of the chelon. However, it is more suitable, for practical purposes, to employ the reciprocals of the stepwise acid dissociation constants, that is to say the stability constants of the "proton complexes" of the chelon. For a tetraprotic acid such as EDTA and related chelons, these expressions are

$$K_1 = \frac{[HY]}{(H)[Y]} \tag{4}$$

$$K_2 = \frac{[H_2Y]}{(H)[HY]} \tag{5}$$

$$K_3 = \frac{[H_3Y]}{(H)[H_2Y]} \tag{6}$$

$$K_4 = \frac{[H_4Y]}{(H)[H_3Y]} \tag{7}$$

It should be noted that the numbering of the proton stability constants is the inverse of that of the dissociation constants; i.e., K_4 corresponds to the first dissociation constant, K_3 to the second, etc. From the equations above, one can introduce an expression for the concentrations of all the protonated forms of the chelon appearing in equation (3). When equations (4-7) are combined with equation (3), the result is

$$[Y]^* = [Y] + K_1(H)[Y] + K_2(H)[HY] + K_3(H)[H_2Y] + K_4(H)[H_3Y] \tag{8}$$

completing the substitution to replace all concentration terms other than [Y] on the right side of (8) gives

$$[Y]^* = [Y] + K_1[Y](H) + K_1K_2[Y](H)^2 + K_1K_2K_3[Y](H)^3 + K_1K_2K_3K_4[Y](H)^4 \tag{9}$$

Division of $[Y]^*$ by [Y] and combination with equation (2) gives the desired

expression for α_H

$$\alpha_H = \frac{[Y]^*}{[Y]} = 1 + K_1(H) + K_1K_2(H)^2 + K_1K_2K_3(H)^3 + K_1K_2K_3K_4(H)^4 \quad (10)$$

Equation (10) allows the calculation of α_H for any pH value provided the four protonation constants of the chelon are known. It is convenient and informative to calculate the α_H for a chelon at several different pH values and to plot log α_H versus pH. Figure 1 shows such a plot for EDTA. When α_H at any pH is known, the conditional stability constant can be calculated by combining equations (1) and (2) with the expression for the absolute stability constant to obtain

$$K_{cond} = \frac{[MY]}{[M][Y]\alpha_H} = \frac{K_{abs}}{\alpha_H} \quad (11)$$

or, in logarithmic form

$$\log K_{cond} = \log K_{abs} - \log \alpha_H \quad (12)$$

Note that this equation contains only the normal complexes MY and none of the hydrogen (MHY) or hydroxo (MOHY) complexes which may be formed under extreme pH conditions. It is also of interest to note that the numerical value of α_H is <u>not</u> dependent upon the concentration of Y but, for a given chelon, is determined solely by the pH.

Thus the effect of lowering the pH on the equilibrium between the metal ion and the chelon is reflected in the K_{cond}, which is smaller than

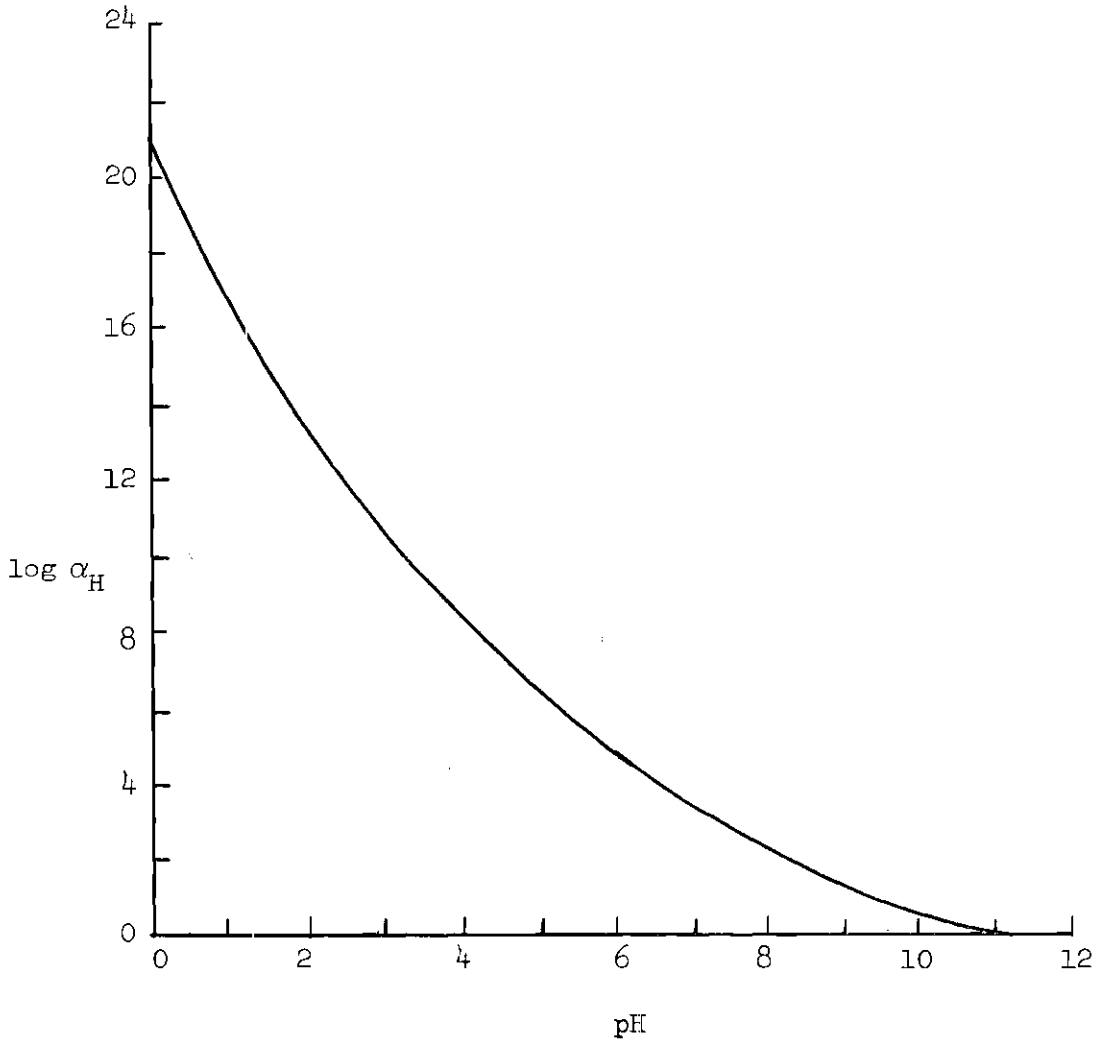

Figure 1. Log α_H for EDTA as a Function of pH

the absolute stability constant. This indicates that at a pH value lower than about 11 the equilibrium

$$M + Y \rightleftharpoons MY$$

is shifted toward the left and the MY concentration at equilibrium is smaller. By using equation (12) as presented above, calculations can be performed which allow the prediction of the effect of pH on the equilibrium between the metal ion and the chelon. For example, the logarithm of the absolute stability constant of the calcium-EDTA complex is 10.7 and the value of log α_H for EDTA at pH 3.0 is 10.6 (11). Thus the logarithm of the conditional stability constant of the calcium-EDTA complex at pH 3.0 as calculated from equation (12) is 10.7 - 10.6 = 0.1. At a pH of 3.0, then, the calcium-EDTA complex is essentially completely dissociated and, for all practical purposes, calcium will not react with EDTA.

The influence of the formation of hydroxo complexes (which is dependent on pH) on the conditional stability constant of the metal-chelon complex is discussed in the next section because the mathematical treatment is analogous to that for auxiliary complex-formers.

The Influence of Other Complex-Formers, the β Factor

When a complex-forming substance other than the chelon is present in the solution, the metal ion in the solution is distributed between the "free" aquated ion and the complexes formed with the chelon and the other complex-forming substance. The conditional stability constant which takes into account the influence of an auxiliary complex-former, Z, is given by

$$K_{cond} = \frac{[MY]}{[M]^*[Y]} \qquad (13)$$

where $[M]^*$ is the concentration of the metal ion not combined with the chelon, this term includes the "free" metal ion concentration as well as that of all the complexes formed with Z. The relationship between $[M]^*$ and [M] is analogous to that given by equation (2) and is given by

$$[M]^* = [M]\beta_Z \tag{14}$$

Assuming that the complexes between the metal ion and Z are mononuclear (i.e., that there is only one metal ion in each complex species), the total amount of the metal ion which is not combined with the chelon is given by

$$[M]^* = [M] + [MZ] + [MZ_2] + ...[MZ_n] \tag{15}$$

The stepwise stability constants for formation of complexes between the metal ion and Z given by

$$K_1 = \frac{[MZ]}{[M][Z]} \tag{16}$$

$$K_2 = \frac{[MZ_2]}{[MZ][Z]} \tag{17}$$

$$K_n = \frac{[MZ_n]}{[MZ_{n-1}][Z]} \tag{18}$$

The elimination by appropriate substitutions from equations (16), (17), and (18) of all terms involving the concentration of the complexes formed by the metal ion and Z gives

$$[M]^{*} = [M] + K_1[M][Z] + K_1K_2[M][Z]^2 + \ldots + K_1K_2\ldots K_n[M][Z]^n \qquad (19)$$

Division by [M] and combination with equation (14) gives

$$\beta_Z = 1 + K_1[Z] + K_1K_2[Z]^2 + \ldots + K_1K_2\ldots K_n[Z]^n \qquad (20)$$

The expression for the conditional stability constant is then obtained from a combination of equations (13) and (14) with the expression for the absolute stability constant. The result is

$$K_{cond} = \frac{[MY]}{[M][Y]\beta_Z} = \frac{K_{abs}}{\beta_Z} \qquad (21)$$

or, in logarithmic form

$$\log K_{cond} = \log K_{abs} - \log \beta_Z \qquad (22)$$

It should be noted that [Z] is the concentration of the "free" ligand, that is, the ligand not combined with the metal ion or bound as a proton complex. The total concentration of Z can be taken to be equal to [Z] only if a sufficient excess is present, and the pH is such that the amount of Z combined with the metal and held as the proton complex may be neglected. It is important to realize that Z may be, and most often is, the conjugate base of a weak acid or a base (e.g., acetate, ammonia, hydroxide) so that the concentration of free Z, [Z], depends upon the pH. This effect can be easily calculated from the appropriate α_H for Z as

shown in the previous section.

If several complex formers are present in the solution, the overall β factor can be calculated according to

$$\beta_{total} = \beta_1 + \beta_2 + \ldots\ldots + \beta_p + (1 - p) \qquad (23)$$

where p is the total number of complex-formers in solution (11). Usually one or two of the factors will be significantly larger than the others and these other factors can then be neglected.

If both the pH effect and the effect due to the presence of foreign complex-formers must be considered simultaneously, the conditional stability constant is obtained by combining the derivations given above

$$K_{cond} = \frac{[MY]}{[M]^*[Y]^*} = \frac{K_{abs}}{\alpha_H \beta_Z} \qquad (24)$$

or, in logarithmic form

$$\log K_{cond} = \log K_{abs} - \log \alpha_H - \log \beta_Z \qquad (25)$$

Other Influences

The value of the conditional stability constant is also affected by the presence in the solution of other metals which form complexes with the chelon, by the formation of mixed acid or base complexes of the type MHY and M(OH)Y, and by the formation of other mixed complexes of the type MZY. When such side reactions are significant, their influence can be

taken into account with factors which are calculated by methods analogous to those outlined above. For a comprehensive treatment of conditional stability constant calculations and for an extensive tabulation of factors for various side reactions, the reader is referred to the monograph by Ringbom (11).

Stability constants for metal-chelon complexes are usually measured at a specified ionic strength (usually 0.1) and temperature (usually 20° or 25°C). By changing these parameters, the chemist can, within a narrow range, change the value of a stability constant. For example, the addition of an inert electrolyte usually decreases the conditional stability constant of a metal-chelon complex. The addition of water soluble organic solvents to the solution also changes the conditional stability constant somewhat. At the present time, our knowledge is not sufficient to allow quantatative predictions regarding these effects. These effects are generally small; however, under certain circumstances they can become quite large. A later section will discuss these effects in more detail.

Selectivity in Chelometric Titrations

A selective reagent is one which reacts with only a limited number of substances under a certain set of conditions. A selective titration reaction can occur only if the reactions of the titrant with foreign metal ions is prevented or suppressed. There are two general approaches used to achieve selectivity for a chelometric titration. The first is the selection of a chelon which is intrinsically more selective for the metal to be titrated. However, this approach is not generally applicable since all chelons of practical importance react to a greater or lesser degree

with the majority of metal ions. The second approach involves the use of a particular chelon and the control of pH, the use of masking agents or kinetic effects, the variation of the mode of titrant addition or method of end point detection, or some combination of these.

The use of α and β factors as presented in the previous sections allows one to predict the effects of reaction conditions on selectivity. Two metals will only react in discrete steps if the conditional stability constants of their chelonates differ considerably. It is then only necessary to be able to detect the end point of the titration of the first reacting metal in order to determine it in the presence of the other metal. This would, however, require that a set of selective or specific indicators be available for each mixture to be titrated. This requirement is met for a very few mixtures, but, in general, is difficult to fulfill. The only alternative is recourse to an instrumental method of end point detection.

The pH Effect

As mentioned previously, a change in pH often affects the relative stabilities of metal chelates. At a low pH the conditional stability of some metal-chelate complexes is reduced to such a degree that the metal complex is essentially completely dissociated. Under these pH conditions, other metals which form stable metal-chelate complexes can be successfully titrated. Thus the selectivity of the complexation reaction is enhanced. For example, one group of metal ions, Bi(III), Fe(III), Cr(III), V(III), and Th(IV) form such stable EDTA complexes that practically no dissociation occurs even at pH 2. For the titration of a metal N in the presence of a metal M using a visual type of indicator, the stability constants

should differ by about 8-10 units in log K (13). It is necessary that K_{cond} for the metal M be lowered sufficiently so that essentially no M reacts with the chelon. In order to illustrate this principle, consider the conditional stability constants of iron(III)-EDTA and calcium-EDTA shown in Figure 2 as a function of pH. These data are taken from Ringbom (11) and are calculated by using the α_H factor and include corrections for the formation of metal hydroxo complexes and mixed complexes of the types MHY and M(OH)Y. Figure 3 shows a plot of log $K_{cond\ Fe(III)\text{-}EDTA}$ - log $K_{cond\ Ca\text{-}EDTA}$ ($\Delta(\log K_{cond})$) versus pH. At pH 10, the difference in the conditional stability constants is only 3.8 log units. At pH 3, however, the difference is 14.0 log units and a selective titration of iron in the presence of calcium is readily possible.

Masking

Since a considerable portion of the present study deals with this topic, it is discussed in some detail in Chapter II.

Kinetic Effects

If the reaction between a metal ion and a chelon is slow under certain conditions, it is possible to take advantage of this kinetic phenomenon for a titration. For example, nickel reacts slowly with EDTA at room temperature, but the reaction is not quite slow enough to allow the "kinetic masking" of nickel. However, if the solution temperature is lowered to 0°C, the decrease in the reaction rate of nickel with EDTA is sufficient to prevent its complexation with EDTA during the period required to titrate another metal ion (14). Similarly, chromium(III) reacts quite slowly with EDTA in solution while iron(III) reacts quickly. Thus iron can be titrated in the presence of chromium (15) although the stability

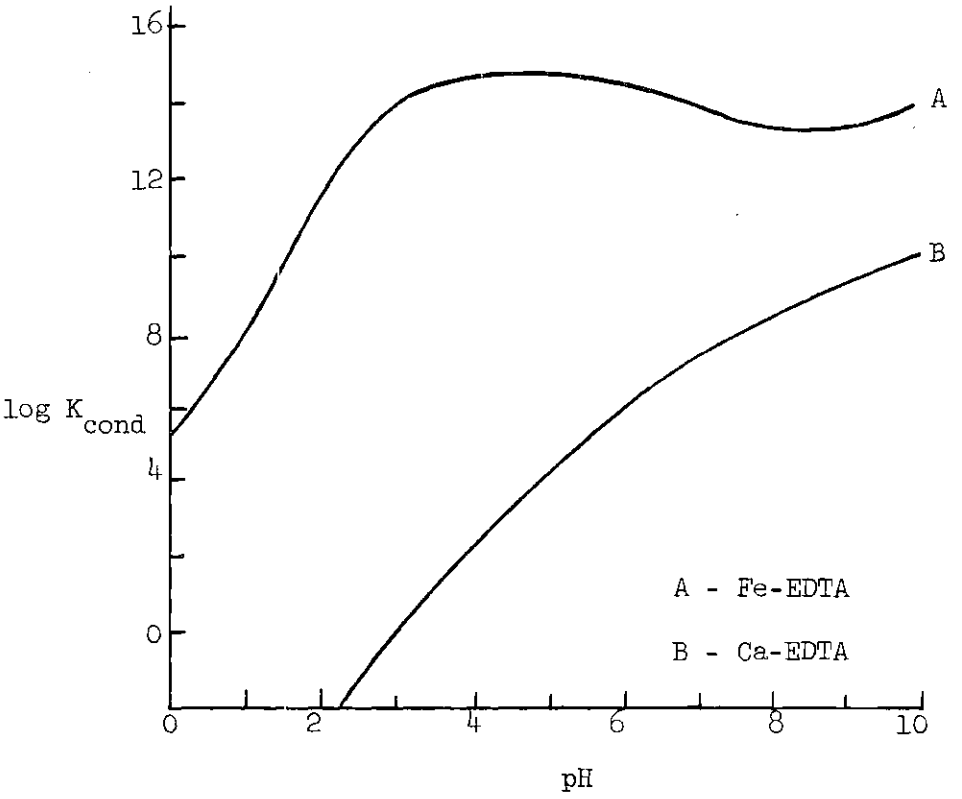

Figure 2. Effect of pH on the Conditional Stability Constants of Fe(III)-EDTA and Ca-EDTA

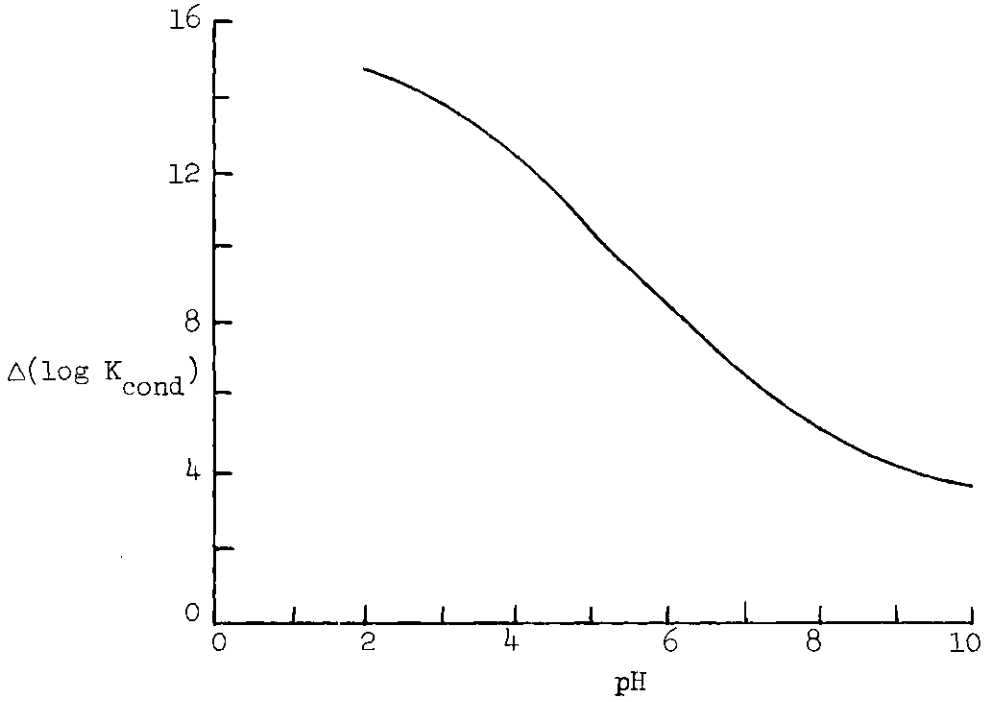

Figure 3. Effect of pH on the Difference Between log K_{cond} for Fe(III)-EDTA and Ca-EDTA

constants of chromium(III)-EDTA and iron(III)-EDTA are nearly equal.

Types of Titrations

Direct Titration. The most frequent approach to chelometric titrations is the direct addition of increments of a standard solution of the chelon to the sample solution until the end point is reached.

Back Titration. When it is necessary to titrate a metal under conditions such that the metal would be precipitated (e.g., as the hydroxide) or when no suitable indicator the the metal is available, a back titration procedure may be employed. In this procedure, an excess of a standard chelon solution is added to the sample solution and the chelon remaining uncomplexed is titrated with a standard solution of a suitable metal ion. A back titration can also be applied when the reaction between the metal ion and the chelon is too slow to permit a direct titration. First, an excess of the chelon is added, the solution is then allowed to stand or it is warmed to complete the complexation, and the excess of chelon is titrated.

Replacement or Substitution Titrations. If a metal does not form a stable complex with a chelon, or if no suitable indicator is available, a replacement or substitution procedure can sometimes be used. In a replacement titration, a solution of a metal ion is treated with an excess of a metal complex which is less stable than the same complex of the metal to be determined. The metal of the added complex is quantitatively displaced and can then be titrated with a standard chelon solution. For example, this method can be used for silver which does not form a chelonate stable enough to permit a direct titration. If $K_2Ni(CN)_4$ is added in excess to a solution containing silver, nickel is quantitatively released

according to

$$2Ag^{+} + Ni(CN)_4^{-2} = 2Ag(CN)_2^{-} + Ni^{+2}$$

The nickel released is then titrated with EDTA (16). The same technique can also be used for metals which form complexes with the chelon. An excess of the chelonate of another metal of lower stability is added and the exchange takes place according to

$$M + NY = MY + N$$

The released metal, N, can then be titrated.

Method of End Point Detection

The selectivity of a titration procedure can sometimes be enhanced by a suitable choice of the method of end point detection. This comes about because some methods of end point detection are inherently more selective than others and their application allows a relaxation of some of the requirements for a successful visual titration. This subject is discussed in some depth in Chapter III.

CHAPTER II

MASKING

Introduction

Masking is by far the most important means of achieving selectivity in chelometric titrations and many other analytical methods. Masking is the process by which one or more particular reactions of a substance are prevented by the addition of a reagent which transforms this substance into a species which no longer undergoes these reactions. The term masking implies that neither the substance being masked nor its reaction product(s) with the masking reagent is physically separated from the solution. Since this work is concerned mainly with chelometric titrations, the following discussion will be confined to masking procedures useful for such titrations.

Masking Procedures

The masking of a particular metal ion in a mixture can be accomplished by one or a combination of two or more of the following processes: 1) precipitation, 2) oxidation, 3) reduction, and 4) complexation.

Precipitation of interfering substances has not been widely applied as a masking process because of the complications due to coprecipitation and postprecipitation phenomena. The most outstanding example of this type of masking is the exclusion of magnesium as the insoluble hydroxide to allow the selective titration of calcium (4). An additional example is the

suppression of interferences from small amounts of heavy metals by the addition of hydrogen sulfide or diethyldithiocarbamate when determining the hardness of water (17).

Where a metal in its higher oxidation state forms a weaker complex or no complex at all with a chelon, masking can be achieved by converting the metal from the lower to the higher oxidation state. Such is the case for chromium(III) which can be masked by oxidation to chromate which does not interfere in the titration reaction (18).

Similarly, where a metal in its lower oxidation state forms a weaker complex with a chelon, as is frequently the case, masking can be achieved by converting the metal from the higher to the lower oxidation state. In some cases, copper can be masked by the addition of ascorbic acid or hydroxylamine which reduce Cu(II) to Cu(I), which does not interfere in the titration reaction. Reduction is especially useful for the masking of iron since the logarithms of the absolute stability constants of the iron(II) and the iron(III)-EDTA complexes are 14.3 and 25.1, respectively (11).

Masking by precipitation is often subject to complications, and the number of metals that can be masked by changing their oxidation states is limited. Consequently, the number of cases to which these types of masking can be applied is restricted. On the other hand, the number of complexation reactions useful for masking is quite large and, for this reason, complexation is most widely employed for masking.

Masking via complexation involves the formation of soluble complexes. (The formation of insoluble complexes is best classified as a precipitation reaction.) As applied to chelometric titrations, this consideration im-

plies that the masking reagent must decrease the conditional stability constant of the chelon complex of the interfering metal ion to such a degree that this ion no longer interferes with the titration. For the purpose of a chelometric titration, it is not mandatory that masking be carried so far as to completely exclude a reaction between the interfering metal ion and the titrant. Actually, the only necessary requirement is that the interfering metal ion does not prevent the desired titration reaction. The ratio of the conditional stability constant of the complex of the metal ion to be titrated to that of the complex of the interfering metal ion is, as a first approximation, the criterion for the feasibility of a selective titration. Thus it is sufficient to reduce the conditional stability constant of the interfering metal ion to such a degree that this ratio becomes large enough to allow a selective titration. The term "masking" as applied to a chelometric titration may then be modified from the strict definition which requires that "the reaction between the chelon and the interfering metal ion be completely excluded" to a definition which requires that "the metal to be titrated react preferentially with the titrant." Thus masking may actually be so weak that a "masked" metal ion may be determined in a subsequent titration.

One of the most versatile masking agents is the cyanide ion (19, 20) with which the cations of cobalt, nickel, copper, mercury, zinc, cadmium, and the platinum metals can be masked to allow the titration of magnesium, calcium, the lanthanides, manganese, lead, indium, and other metals which do not form stable cyanide complexes. A most useful aspect of the application of cyanide ion is that zinc and cadmium can be liberated from their weak cyanide complexes by treatment with formaldehyde or chloral

hydrate (21). Both aldehydes react with cyanide to form cyanohydrins, decomposing the cyanide complexes of zinc and cadmium, but not those of the other metals mentioned above. This process of masking with cyanide and selective demasking using formaldehyde or chloral hydrate makes possible a whole series of sequential determinations. Other masking reagents which operate through complex formation are Tiron and triethanolamine which have been used to mask aluminum and titanium (22,23); and iodide which has been used in low concentrations to mask mercury almost specifically.

Cheng (24) has reviewed the applications of masking reagents and presented some principles which can be used in their evaluation.

Low Stability Masking

One type of masking which has only recently been investigated and which makes up a considerable portion of this work is "low stability masking". Generally, masking by complexation as described above is accomplished by the addition of masking reagents that form rather strong complexes with the interfering metal ion(s). Consequently, only moderate concentrations of these reagents are necessary to mask these ions. On the other hand, "low stability masking," as the name implies, involves the addition of reagents which form relatively weak complexes with the interfering metal ion(s), and thus requires a high concentration of this reagent in order for masking to be effective.

The first and, until recently, only example of "low stability masking" was the prevention of an interference by thorium in the titration of the rare earths and some other metals (25). The masking was accomplished

by the addition of large amounts of sodium sulfate. One reason this type of masking has received little attention is that, under normal circumstances, titrations are not carried out in such concentrated solutions as are necessary for a masking effect to be observed. Also, the usual calculations based on complex equilibria in dilute aqueous solutions cannot be applied precisely at such extreme concentrations, and an adequate masking effect is not predicted when such calculations are made. These calculations are commonly based on approximations which are permissible for dilute aqueous solutions and involve concentrations rather than activities. If solutions contain high concentrations of a weak complexing reagent, however, such approximations are no longer valid and the results obtained may be highly misleading. For example, suppose the conditional stability constants of the zinc and cadmium-EDTA complexes in solutions containing high concentrations of iodide are calculated using the necessary β factors obtained by employing equations (20) and (21) of Chapter I. In order for masking to be effective, the ratio of the calculated conditional stability constant of the zinc-EDTA complex to that of the cadmium-EDTA complex should be 10^7 or greater for a visual titration (see Chapter III). The ratio actually obtained from such calculations is very small (about 10^1). Thus, no masking of cadmium by iodide would be predicted. However, Flaschka and Butcher (26) have successfully masked cadmium with iodide for the visual titration of zinc. The fact that masking is observed for this system strikingly demonstrates the impossibility of extending calculations valid for dilute aqueous solutions to the concentrated solutions necessary for "low stability masking".

In such concentrated solutions, the activities of both the complex-

ing reagents and the metal ions will be changed to such a degree that the approximation of these activities by use of concentrations is no longer valid. While it might be theoretically possible to obtain a useful result from calculations involving activities, the necessary activity coefficients are not known, and thus any predictions as to the possible application of "low stability masking" must at the present time be made on a strictly empirical basis.

Solutions containing such high concentrations of weak complex formers may actually no longer be "aqueous" in character. In aqueous systems, an exchange reaction takes place between the water molecules coordinated about the metal ion and the chelon, and the extent of this exchange reaction determines the stability constant of the metal-chelon complex. However, in such concentrated solutions as are necessary for "low stability masking", the metal ion is in a much different environment than in a truly aqueous solution, and, from the point of view of the metal ion, the solution may well be non-aqueous, since the solvation sphere of the metal ion is partially or completely occupied by species other than water. The stability constant of the metal-chelon complex in this case depends upon the extent of exchange between the species occupying the solvation sphere of the metal ion and the chelon. The stability of the metal-chelon complex under those conditions would have no relationship to the stability of the same complex in an aqueous environment since the extent of the exchange reaction for this system would probably differ greatly from that for an aqueous system. Thus predictions as to the feasibility of "low stability masking" made on the basis of stability constants determined in dilute aqueous solutions are not valid.

Partial Masking

In all the types of masking discussed thus far the masking reagent was added at least in an amount equivalent to that of the substance to be masked. In practice, this reagent is usually added in a moderate excess and, in the case of "low stability masking," in a considerable excess. Many practical cases exist where a small amount of a foreign substance has no effect on the reaction under consideration, and interference occurs only if the amount of this foreign substance exceeds a certain level. Thus, in such cases, a new masking process termed "partial masking" seemed possible. The statement that a substance is only "partially masked" indicates that the masking reagent is added to such an extent as to decrease the concentration of the foreign substance to or below the level at which it starts to exert an interference. Such "partial masking" would allow the application of masking reagents which cannot be added in excess as in the normal procedure because they would also mask the substance to be determined. This situation can be treated as follows. If a solution contains a metal N and an interfering metal M, "partial masking" may be applied if the stability constant of the complex MY formed by the metal M and the ligand Y is larger than that of the corresponding complex NY formed by the metal N and the ligand, and if the procedure for the determination of the metal N with which the "partial masking" technique is to be applied is applicable in the presence of a reasonable excess of the metal M before the addition of any masking reagents.

The application of "partial masking" is not undertaken in order to completely mask the metal M but to reduce the molar ratio of "free M":N to some value at which the procedure for the determination of N can be success-

fully applied.

Consultation with compiled tables of stability constants for complexes of various metals with a given ligand may be undertaken to determine whether "partial masking" might be applied to a particular system. However, even in favorable cases, only an approximate prediction can be made as to the applicability of "partial masking" from the difference in stability constants of the complexes of the metals in question. Obviously no quantitative prediction as to the fraction of the metal N left uncomplexed can be made by use of stability constants alone since the fraction of this metal left uncomplexed depends upon several factors.

1. The ratio of the conditional stability constant of the complex MY to that of the complex NY (i.e., K'_{MY}/K'_{NY}).

2. The fraction of the concentration of the metal M added as ligand.

3. The concentration of the metal M relative to that of the metal N.

The ratio K'_{MY}/K'_{NY} is, of course, of primary importance. If this ratio is large, the ligand will be held almost completely by the metal M leaving the N uncomplexed. If, however, this ratio is small, a large fraction of the N present will be held by the ligand. Calculations were undertaken to evaluate the relative importance of each of these factors and to obtain a quantitive basis for determining the usefulness of the "partial masking" technique for various systems. These calculations are presented below.

If the stability constants of the metal complexes MY and NY are expressed as

$$K'_{MY} = \frac{[MY]}{[M][Y]} \tag{1}$$

$$K'_{NY} = \frac{[NY]}{[N][Y]} \tag{2}$$

the ratio of these two constants, Q, is then

$$Q = \frac{K'_{MY}}{K'_{NY}} = \frac{[MY]}{[N]} \cdot \frac{[N]}{[NY]} \tag{3}$$

The material balances for the system which contain N, M, and Y are

$$C_M = [MY] + [M] \tag{4}$$

$$C_N = [NY] + [N] \tag{5}$$

$$C_Y = [MY] + [NY] + [Y] \tag{6}$$

where C_M, C_N, and C_Y are the total concentrations of these species in all forms. If, as is normally the case, the complexes MY and NY are sufficiently stable (i.e., K_{MY} and K_{NY} are large) and $C_M > C_Y$ it may be assumed that [Y] is very small and thus equation (6) will reduce to

$$C_Y = [MY] + [NY] \tag{7}$$

In order to simplify further calculations, the following definitions are introduced

$$C_M = C \tag{8}$$

$$C_Y = PC \tag{9}$$

where P is a fraction less than or equal to one ($P \leq 1$)

$$C_N = TC \tag{10}$$

where T is a small number defined as $T = C_N/C_M$.

The ultimate purpose of this calculation is the derivation of an expression for the fraction of the metal N left "free" in the presence of a large amount of the metal M which has been partially complexed by the ligand Y. If this fraction is expressed as

$$F = [N]/C_N \tag{11}$$

where [N] is the concentration of uncomplexed or "free" N, and if this expression is combined with equation (10), the result on rearrangement is

$$[N] = FCT \tag{12}$$

In order to calculate Q as defined in equation (3) in terms of the variables C, F, P, and T, expressions for [N], [NY], [MY], and [M] containing these variables must be introduced. Rearrangement of equation (5) to $[NY] = C_N - [N]$ and substitution for C_N and [N] from equations (10) and (12) gives

$$[NY] = CT - FCT \tag{13}$$

Similarly, equation (7) rearranges to $[MY] = C_Y - [NY]$ and substitution for C_Y from equation (9) gives

$$[MY] = PC - [NY] \tag{14}$$

Substituting the expression for [NY] from equation (13), equation (14) becomes

$$[MY] = PC - CT + FCT = C(P - T + FT) \tag{15}$$

Rearrangement of equation (4) to $[M] = C_M - [MY]$ and substitution for C_M and MY from equations (8) and (15) gives

$$[M] = C - PC + CT - FCT = C(1 - P + T - FT) \tag{16}$$

On substitution of the expressions for [N], [NY], [MY], and [M] as given by equations (12), (13), (15), and (16) into equation (3), the expression for Q becomes

$$Q = \frac{[MY]}{[M]} \cdot \frac{[N]}{[NY]} = \frac{(P - T + FT)}{[(1 - P + T) - FT]} \cdot \frac{F}{(1 - F)} \tag{17}$$

It should be noticed at this point that the concentration term has dropped completely out of the expression. Thus the fraction of the metal N "free" does not depend upon the concentration of M or N but only upon $T(C_N/C_M)$,

P, and Q. Although equation (17) fully defines the relationship between F and the other variables, calculation of this quantity for various conditions is cumbersome, since the equation is quadratic in F. A more useful equation would be one which expresses F as a function of Q, P, and T. Rearrangement of equation (17) into the form of a quadratic in F gives

$$(Q - 1)T\,F^2 - [Q(1 - P + T) + T(Q - 1) + P]F + Q(1 - P + T) = 0 \qquad (18)$$

Solution of this equation for F gives

$$F = \frac{[\,] \pm \sqrt{[\,]^2 - 4(Q - 1)T\,Q(1 - P + T)}}{2(Q - 1)T} \qquad (19)$$

where [ ] represents [Q(1 - P + T) + T(Q - 1) + P]

If no ligand is added (i.e., P = 0), all the metal N is free and F = 1. Application of this limiting condition to equation (19) reveals that the proper sign before the root is negative and the equation then becomes

$$F = \frac{[\,] - \sqrt{[\,]^2 - 4(Q - 1)T\,Q(1 - P + T)}}{2(Q - 1)T} \qquad (20)$$

By means of this equation, it is possible to calculate F for any values of K_{MY}, K_{NY}, P, and T. In order to verify this equation, F can be calculated at a value of Q = 1 (i.e., $K_{MY} = K_{NY}$) for a small value of T. Under these conditions, it would seem that the same fraction of the total amount of N as of M would be complexed since both M and N have the same probability

of combining with the ligand. Equation (18) upon substitution of Q = 1 reduces to

$$- F(1 - P + T) - FP + (1 - P + T) = 0$$

which upon simplification and rearrangement reduces to

$$F = \frac{(1 + T) - P}{(1 + T)} = 1 - \frac{P}{1 + T} \tag{21}$$

If T is very small (i.e., $T \ll 1$), equation (21) becomes

$$F = 1 - P \tag{22}$$

which corresponds exactly to the expected result.

Since it is somewhat tedious to calculate F for each and every value of Q, P, and T, it was decided to calculate F as a function of P for selected values of Q and T and to record the results in graphical form. The resulting curves, in addition to supplying the value of F at any value of P, show the variation of F with P at constant Q and T, and by comparison of different curves the variation of F with Q at constant P and T. Graphical representations of F versus P in the range P = 0.8 - 1.0 for $T = 1 \times 10^{-4}$ and for $Q = 10^{1.0}$, $10^{1.5}$, $10^{2.0}$, $10^{2.5}$, $10^{3.0}$, $10^{4.0}$ are presented in Figure 4. As might be expected, these curves show that for low values of Q (i.e., $10^{1.0}$), the values for F in the range P = 0.8 - 1.0 are quite low. Thus, a considerable portion of the metal N would be

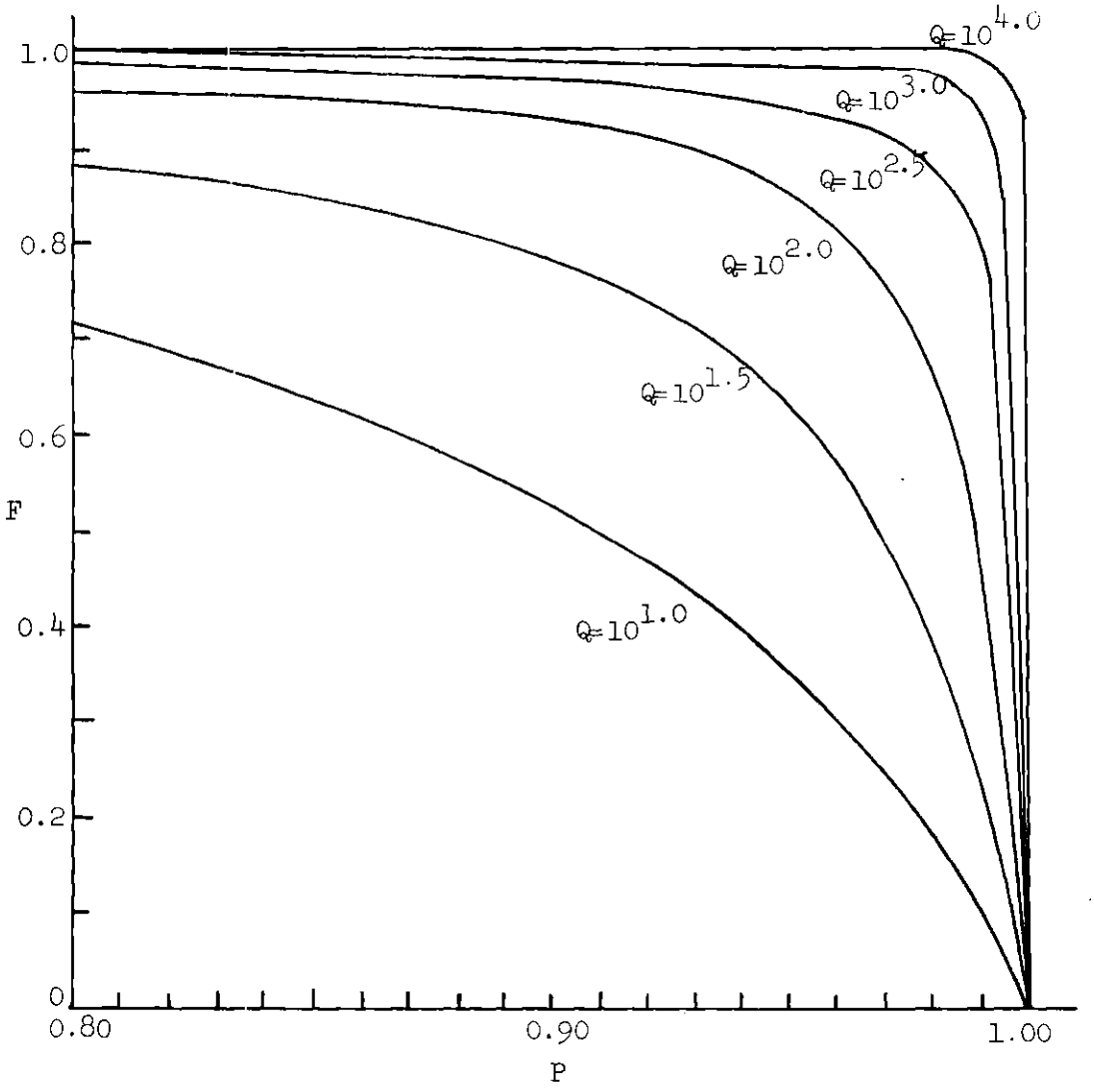

Figure 4. Fraction of the Metal N Free as a Function of P

present as the NY complex under these conditions. As Q becomes larger, the amount of N "free" increases until at $Q = 10^{4.0}$ the value for F is 0.99 when P = 0.99. Thus, under these conditions, 99 percent of the N present remains uncomplexed when the ratio of "free M" : N has been reduced from 10,000:1 to 100:1.

The derivation of equation (20) was considerably simplified by making the assumption that no complexing reagent other than the "partial masking" reagent was present in the solution. However, in many practical cases, a "partial masking" approach might be advantageous for photometric or extractive procedures which involve the addition of a second complexing reagent. In this case, the results of calculations based on equation (20) may not be valid. The second complexing reagent may lead to a more favorable situation with regard to the fraction of N left uncomplexed by the "partial masking" reagent. If the second reagent forms a more stable complex with N than with M, the equilibrium of the system may be shifted in such a manner that a "partial masking" procedure may be applied even though calculations utilizing equation (20) indicate that such a procedure would be impractical. If, however, the second reagent forms a more stable complex with M, the situation may be reversed, and the fraction of N left uncomplexed may be smaller than that calculated. Also, the reaction of the second reagent with either M or N may be favored kinetically, and a shift in equilibrium contrary to that predicted on the basis of the relative stabilities of their complexes may take place.

In order to fully describe such a system, the derivation of an equation which takes into account the effect of the second reagent on the sys-

tem would be necessary. However, equation (20) provides a sufficient amount of information to allow an adequate prediction to be made in most cases, and no additional derivation seems to be necessary.

CHAPTER III

METHOD AND SELECTIVITY OF END POINT DETECTION

Introduction

The method of end point detection was listed in Chapter I as one of the factors which could be varied in order to achieve selectivity in a chelometric titration. Generally, methods of end point detection can be divided into two distinct groups: visual detection and instrumental detection. Each type of end point detection will be discussed in detail in this chapter.

Visual Detection of End Points

The visual detection of an end point in the majority of chelometric titrations depends on the recognition of the change in color which occurs when a metal ion is removed from its indicator complex by the addition of a chelon. There are only a few types of compounds which can be successfully used as indicators for chelometric titrations. These indicators include azo and triphenylmethane dyes, phthaleins and sulfonphthaleins, and phenolic compounds (27) which form colored complexes with metal ions.

Chelometric titrations resemble acid-base titrations as far as the role of the indicator in the titration is concerned. However, the theoretical treatment of the relevant equilibria for metal indicators is much more involved than for acid-base indicators. In an acid-base titration, a pH sensitive indicator is used. A proton is attached or released by the indicator within certain pH range; the exact reaction depending on

whether the pH range is approached from a higher or lower pH. The protonized form of the indicator differs in color from the unprotonized form, and a color change takes place as the pH range is traversed. In a chelometric titration, a pM sensitive indicator is used. The metal ion, in this case, is attached or released by the indicator in a particular pM range; the exact reaction depending on whether the pM range is approached from a higher or lower pM. Since the metalized form of the indicator differs in color from the unmetalized form, the complexation reaction is accompanied by a color change. In both chelometric titrations and acid-base titrations, the plot of pM or pH versus the volume of titrant added yields a logarithmic titration curve with the end point at the inflection point of this curve. Therefore, one desires an indicator whose pM or pH range is located in the steepest part of the respective titration curves. The ideal condition is obtained when the midpoint of the color change interval occurs at the inflection point of the titration curve.

The pH range within which a certain pM sensitive indicator can be employed for a chelometric titration is, generally, somewhat limited. Since most pM sensitive indicators (often called metal indicators or metallochrome indicators) and their metal complexes are also acid-base indicators, the pH of a chelometric titration employing these indicators must be carefully controlled. Most metal indicators are also nonspecific which creates a problem if a foreign metal ion in the sample solution reacts with the indicator. The effects of acid-base and complexation side reactions of metal indicators can be handled by calculations which involve the use of the appropriate α and β factors.

Visual chelometric titrations can be considered to be logarithmic

titrations, since indicators respond to changes in pM. The precision of the detection of the end point depends greatly on the magnitude of the change in pM around that point. In favorable cases, the pM at which the metal indicator changes color can lie anywhere within a wide pM range, since this range is equivalent to only a very small volume of titrant. As the concentration of the metal ion is lowered or as the conditional stability constant of the metal chelonate is decreased, the pM jump at the end point becomes smaller, and the requirements for the pM range of the metal indicator become more stringent.

In order to obtain a sharp end point, the ratio of the stability constant of the metal-chelon complex to the stability constant of the metal-indicator complex must be on the order of 10^4. Also, the value of the metal indicator stability constant must be greater than about 10^5. These limits are obtained from theoretically derived expressions after some simplifying assumptions are introduced (13). All the stability constants mentioned above are, of course, conditional stability constants.

The selective, visual titration of a metal N in the presence of a metal M, when using an indicator, I, which is specific for N, is possible when

$$\frac{K_N}{K_M} \geq \frac{K_I}{10^{-2}} \qquad (1)$$

K_M and K_N are the conditional stability constants of the metal chelonates and K_I is the stability constant of the metal-indicator complex (28). Since, as mentioned above, K_I must be at least 10^5, it follows from equa-

tion (1) that the ratio K_N/K_M must be greater than about 10^7 if the metal is to be selectively titrated to a visual end point.

The pM change at the end point of some chelometric titrations results in a change in the potential of the redox couple formed by the titrated metal and an equilibrium concentration of its reduced or oxidized species in solution. This potential change can sometimes be detected visually by the change in color of a redox indicator. These redox indicators have found only limited application, however, because of their sensitivity to small amounts of oxidizing and reducing impurities in the sample solution. Also, only a small number of redox indicators suitable for chelometric titrations are known. Thus, only a few applications of this type or indicator have been developed (27).

Instrumental Detection of End Points

Significant advantages are often gained when instrumental detection of the end point for chelometric titrations is employed. If the use of an indicator is avoided, improved selectivity often results. Even when an indicator is present in the sample solution, the replacement of the human eye by a photocell and the use of monochromatic light (photometric titration) often allows a titration to be performed successfully where the visual detection of an end point is impossible. In general, five types of instrumental methods are used for the detection of end points in chelometric titrations: 1) potentiometry, 2) amperometry, 3) conductometry, 4) photometry, and 5) enthalpometry. A few other very limited methods have been applied in special cases.

The five instrumental methods of end point detection mentioned above

can be divided into two distinct groups, namely logarithmic and linear titrations.

The titration curve for a logarithmic titration is obtained by plotting a quantity related to the logarithm of the concentration of one or more of the species participating in the titration reaction versus the volume of titrant added. Examples of this type of titration are acid-base titrations (pH), precipitation and complexation titrations (pM), and redox titrations (cell potential).

The titration curve for a linear titration is obtained by plotting a quantity which is directly proportional to the concentration of one or more of the species participating in the titration reaction versus the volume of titrant added. Examples of this type of titration are conductometric titrations (conductance), amperometric titrations (diffusion current), thermometric titrations (temperature), and photometric titrations (absorbance).

The end point of a logarithmic titration is located at the inflection point of the S shaped titration curve. The end point of a linear titration is found at the point of intersection formed by the extrapolation of the two essentially straight line portions of the titration curve. In order to compare the two types of end point detection and to understand their practical implications, a complexation reaction will be taken as an example.

For the complex equilibrium, $M + Y = MY$, the highest degree of dissociation occurs when M and Y are present in equivalent amounts, that is, at the equivalence point and, therefore, near the end point. Thus, the end point for a logarithmic titration is located in the portion of the

curve which is the worst with respect to dissociation. Using a linear titration for the same system, one branch of the titration curve is established well before the end point. The titrated metal, M, is present in excess in this region, and the equilibrium is shifted to the right to favor complete reaction of the metal with the titrant. Thus, any change in the measured property will be essentially proportional to the amount of titrant added and a straight line is obtained. In the same manner, beyond the end point the titrant, Y, is present in excess and a shift towards the right favors complete reaction of the metal with the titrant. Again, a straight line is the result. The portion of the titration curve in the vicinity of the end point may have a considerable amount of curvature due to the dissociation of the complex. This portion is not used, instead, the two straight line portions before and after the end point are extrapolated and the intersection of these two lines is taken as the end point. Due to the fact that the data for a linear titration are extrapolated from the two extremes of the titration curve where the equilibrium is most favorable, the requirements with respect to complex stability for a successful linear titration are much less stringent than for a logarithmic titration.

Calculation of Titration Curves

The course of a chelometric titration is usually illustrated by means of a titration curve which plots pM (i.e., - log [M]) as a function of the volume of titrant added.

The main difficulty in calculating such curves is taking into account the influence of various side reactions. If conditional stability constants are used, this difficulty can be avoided, and the calculation

is considerably simplified. The theoretical titration curve can then be obtained by solving a series of simultaneous equations which, for chelometric titrations, are composed of the stability constant expression

$$K_{cond} = \frac{[MY]^*}{[M]^*[Y]^*} \tag{2}$$

and the conservation expressions

$$C_M = [M]^* + [MY]^* \tag{3}$$

$$C_Y = [Y]^* + [MY]^* \tag{4}$$

For simplicity, the stars (*) will be omitted hereafter. If we define a as the fraction titrated, it can be expressed as

$$a = \frac{C_Y}{C_M} \tag{5}$$

where C_Y and C_M are the total concentrations of these species in all forms. Due to the nature of this calculation, the effect of dilution by the titrant is neglected.

Combining equation (4) with equation (5)

$$a = \frac{[Y] + [MY]}{C_M} \tag{6}$$

Solving (2) for [Y] and substituting into (6) gives

$$a = \frac{\frac{[MY]}{[M]\,K} + [MY]}{C_M} = \frac{[MY]}{C_M}\left(1 + \frac{1}{[M]\,K}\right) \qquad (7)$$

Solving equation (3) for [MY], and substituting into (7) gives

$$a = \left[\frac{C_M - [M]}{C_M}\right]\left[1 + \frac{1}{[M]\,K}\right] \qquad (8)$$

This equation is an exact relationship between a and [M] in terms of the known quantities C_M and K_{cond}. It is possible to solve equation (8) for [M] as a function of a, but for actual calculations it is simpler and more convenient to treat [M] as the independent variable.

Some logarithmic titration curves calculated with the use of equation (8) are presented in Figure 5.

Logarithmic Titrations

The logarithmic titration method most commonly applied to practical systems is the potentiometric titration. Either as a pH titration utilizing a glass indicator electrode or as a pM titration utilizing some other sort of indicator electrode. When a reversible couple can be established between the metal to be titrated and an electrode made of the same metal, or between the metal to be titrated and a reduced form of that metal in solution, the E.M.F. of that couple is given by the Nernst equation

$$E = E^{o} + \frac{2.303\ RT}{nF} \log \frac{[M]_{ox}}{[M]_{red}} \qquad (9)$$

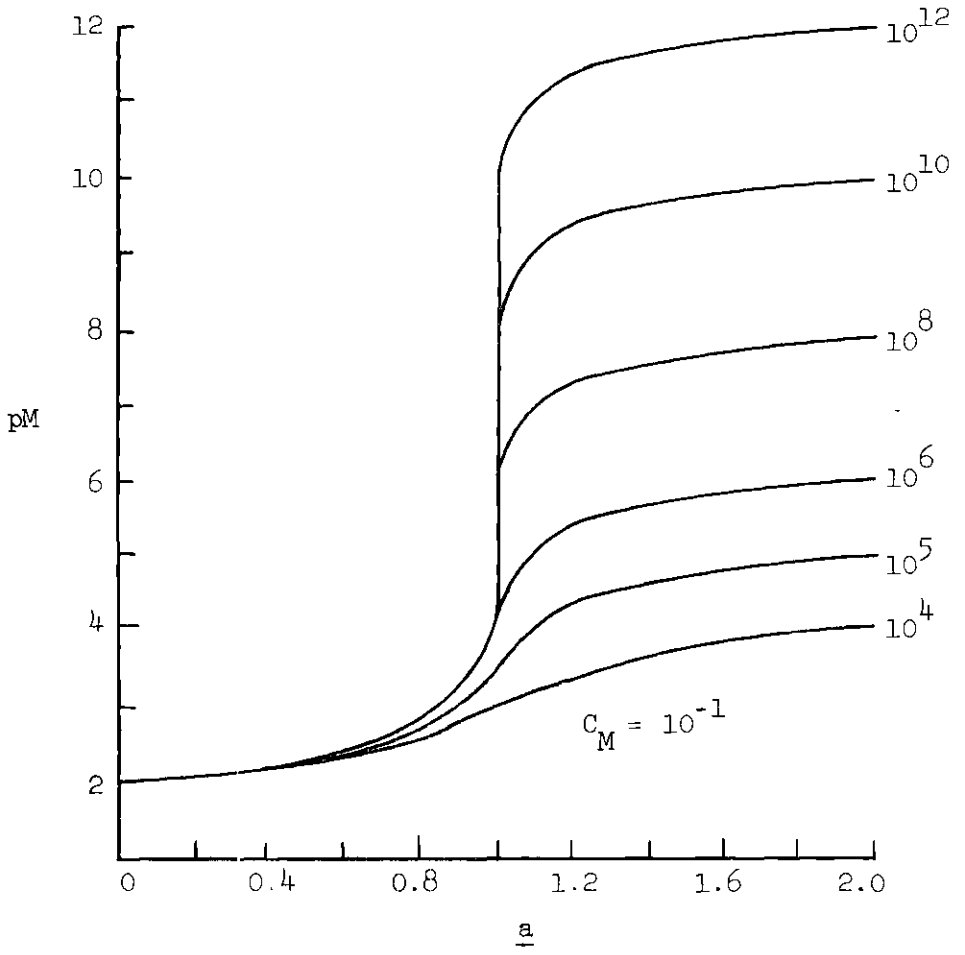

Figure 5. Calculated Logarithmic Titration Curves

If the electrode is made of the metal itself, its activity is considered to be unity and equation (9) reduces to

$$E = E^{o} - \frac{2.303\ RT}{nF}\ pM \qquad (10)$$

If the concentration of the reduced form remains constant during the titration, equation (9) reduces to

$$E = E^{o} - \frac{2.303\ RT}{nF}\ pM_{ox} + \frac{2.303\ RT}{nF}\ pM_{red} \qquad (11)$$

where the term involving pM_{red} is a constant. Thus the measured half-cell potential is directly proportional to pM and the cell voltage curve is analogous to the pM curve.

For the accurate detection of an end point in a potentiometric titration, the E.M.F. jump at the end point must be large. The height of this jump depends on both the metal ion concentration and the value of the conditional stability constant of the complex, MY. A "titration factor", T, defined as (29)

$$\log K_{cond}\ C_{M} = T \qquad (12)$$

furnishes a guide as to which minimum value of the product, $K_{cond}\ C_{M'}$ is required in order to accurately detect an end point. The minimum value of T which will allow a potentiometric or other logarithmic titration to be successfully carried out has been established as about four. The mini-

mum value of T necessary to detect an end point visually is slightly larger than five. Thus it can be seen that the conditions necessary for a successful potentiometric titration are somewhat less stringent than those for a visual titration.

When a foreign metal ion, M, is present in the solution, the effect of competing equilibria can be taken into account by use of the α_M factor. A foreign metal ion has the effect of decreasing the conditional stability of the complex, NY, and, therefore, decreasing the pM jump at the end point. For example, consider the titration curve in Figure 5 with a K_{cond} of 10^{10} in the absence of a foreign metal ion. Assume the same metal is titrated in the presence of a metal M whose concentration is 10^{-2} F and whose chelonate has a conditional stability constant of 10^7. The α_M is given by

$$\alpha_M = 1 + K_{MY}\, C_M = 10^5 \qquad (13)$$

Thus the conditional stability constant of the complex, NY, in the presence of M is $10^{10}/10^5 = 10^5$. The resulting titration curve for $K_{cond} = 10^5$ is also shown in Figure 5.

Linear Titrations

Since a major portion of this work deals with photometric titrations, the discussion of linear titrations is limited to this field. This discussion is presented in the following chapter.

CHAPTER IV

PHOTOMETRIC TITRATIONS

Background

When a beam of monochromatic light is passed through a medium which absorbs light of that wavelength, the intensity of the light beam is decreased. The ratio of the intensity of the emerging light, I, to that of the incident light beam, I^{o}, is called the transmittance of the medium

$$\frac{I}{I^{o}} = T \qquad (1)$$

The transmittance of an absorbing medium has been found to be exponentially related to the length of the light path through the absorbing medium, and to the concentration of the absorbing species in that medium, expressed as

$$T = e^{-kbc} \qquad (2)$$

where k is a constant, b is the path length in centimeters, and c is the concentration of the absorbing species. Upon taking the logarithm to the base 10 and rearrangement equation (2) becomes

$$- \log T = abc = A \qquad (3)$$

where A (- log T) is the absorbance, a is the absorptivity of the absorb-

ing species at the wavelength employed, and b and c are the path length and concentration, respectively. Equation (3) is the Lambert-Beer law for the absorption of monochromatic light and is the basis for spectrophotometric determinations and photometric titrations. The most important consequence of the Lambert-Beer law for spectrophotometric determinations and photometric titrations is the linear relationship between the concentration of the absorbing species in the solution and its absorbance. For a photometric titration, the absorbance is plotted versus the volume of titrant added, and the two linear portions of the curve are extrapolated to their point of intersection which is taken as the end point. The shape of a given titration curve depends on the absorptivities of the species titrated, the titrant, and the reaction products. The wavelength used for the titration is chosen from the absorbance spectra of the species involved in the titration. The wavelength chosen is usually the one at which the greatest possible absorbance change will be obtained during the titration.

Photometric End Points

The shape of a photometric titration curve will vary with the type of photometric indication employed for the titration. A nomenclature for the three types of photometric indications has been proposed by Flaschka and Sawyer (30). Each of these three types will be discussed below.

Self-Indication. A system is said to be self-indicating when, upon addition of titrant, a metal ion initially present as a complex is progressively transferred into a chelonate of differing absorptivity. A linear titration curve, such as the ones shown in Figure 6, curves A and B, is obtained.

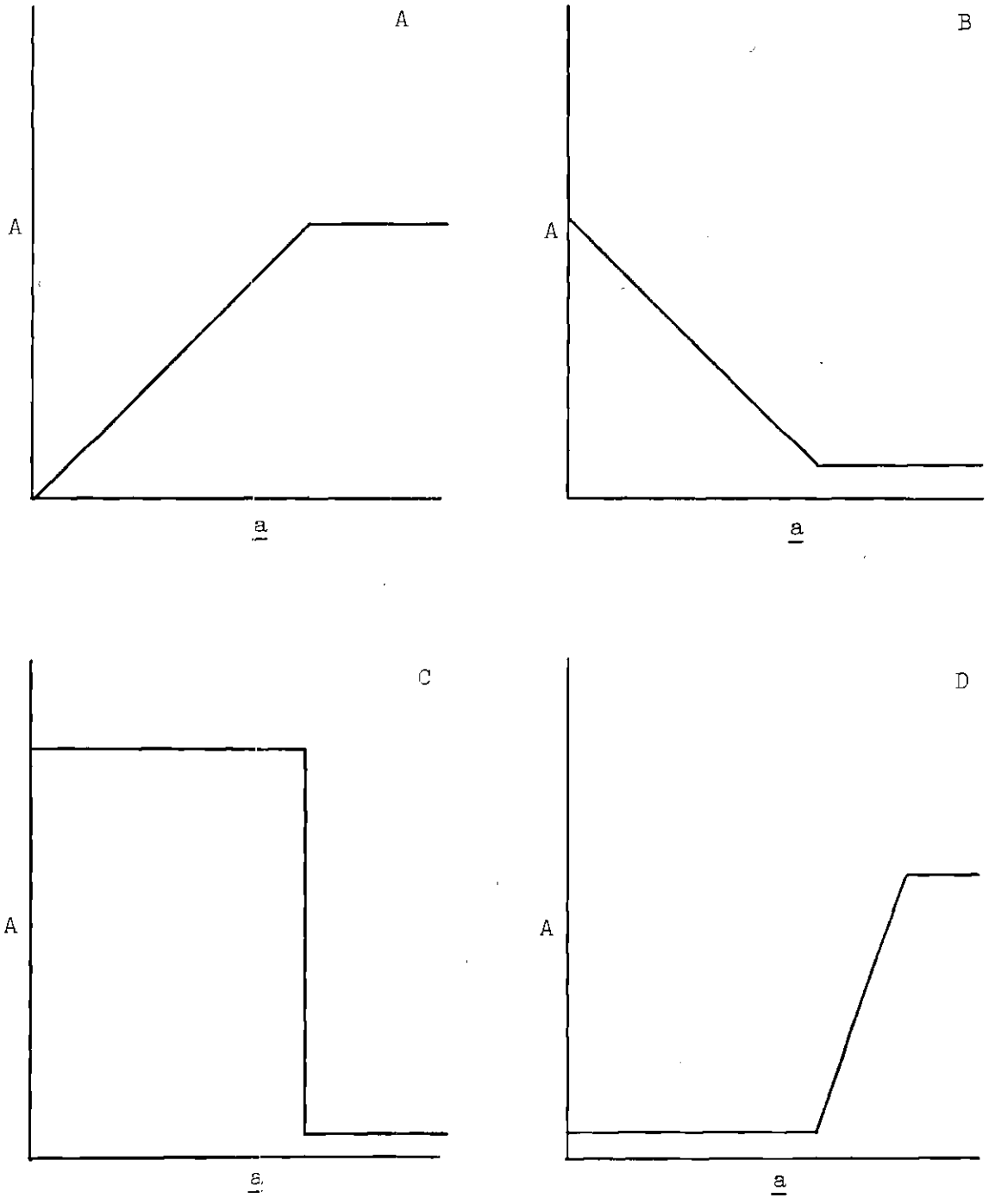

Figure 6. Idealized Photometric Titration Curves for Various Types of Indication

Step-Indication. If a small amount of a complex-forming indicator is employed to form a colored metal indicator complex, a step-like change in absorbance is observed at the end point as shown in Figure 6, curve C. This type of indication is referred to as step-indication. Titrations employing step-indication are linear titrations only with respect to the indicator in that the absorbance is a linear function of the concentration of the free or metalized indicator. However, the indicator responds to the pM jump at the end point. Thus, photometric titrations with step-indication are logarithmic with respect to the metal and linear with respect to the indicator and can be classified as quasilogarithmic titrations. The requirements for successful step-indication are similar to those for visual indication but are generally less stringent.

Slope-Indication. If a metal ion, its titrant, and the complex formed by their reaction are colorless, an end point can sometimes be obtained by adding another metal ion which gives a self-indicating system and forms a less stable complex with the titrant. Thus the metal to be determined is titrated prior to the indicator metal, and the added metal and the titrant form a self-indicating system which locates the end point of the titration. This type of indication is called slope-indication and is illustrated in Figure 6, curve D. The equilibrium requirements for a slope-indicating system are those for a selective linear titration of the metal to be determined. Also, the absorptivities of all the species involved must be such that the slope of the titration curve before and after the end point differ sufficiently to permit precise location of that point.

One of the first systems studied involving slope-indication was the EDTA titration of bismuth using copper as the slope indicator (31). The

titration curve for that system is similar to curve D of Figure 6. The first horizontal segment corresponds to the titration of bismuth. After all the bismuth has been titrated, copper is titrated and the absorbance increases due to the formation of the intensely colored copper-EDTA complex. If the titration is continued, copper can be determined, since, when all the copper has been titrated, a second horizontal segment is obtained which locates the end point for copper. Thus it is possible to determine two metals from a single titration curve.

Applications of Photometric Titrations

Generally, photometric end point detection is advantageous when applied to the titration of dilute solutions or to systems in which the titration reaction is incomplete at the end point, e.g., titrations of very weak acids or bases, complexation reactions forming rather weak complexes, and reactions which are slow in the vicinity of the end point. These systems tend to produce a rounding of the photometric titration curve in the vicinity of the end point, but such rounding is often no hindrance to the application of extrapolative photometric methods.

The application of photometric end point detection to titrations which can also be performed visually increases the precision of the titration but does not necessarily increase the accuracy (32). Photometric titrations can be performed automatically which is an advantage for routine analysis.

Photometric end point detection is also useful for systems in which the human eye cannot detect a visual end point. A photometric end point is often required when strongly colored solutions are to be titrated.

Since essentially monochromatic light is used for photometric titrations, it is possible to choose a wavelength which will be free of interference from the background color of the solution. Photometric end point detection is also useful in cases where the color change is "indistinct or dragging". If the titration reaction is slow or an unfavorable equilibrium exists at the equivalence point, an indistinct end point is obtained. An extrapolative photometric method is applicable in either case. Another possible cause of a poor visual end point lies in the fact that the difference in "color" of the metalized and free form of an indicator may not be detectable to the eye. A phototitrator, however, can usually differentiate between "colors" which appear almost identical to the human eye.

Calculation of Photometric Titration Curves

A crude estimation as to whether or not a reaction can be employed as the basis for a photometric titration can be made from an inspection of the relevant stability constants and the absorption spectra of the species involved in the titration. It is also possible to calculate the entire titration curve using rigorously derived equations. For example, photometric titration curves for acid-base systems have been derived by Goddu and Hume (33) and by Higuchi (34).

Titration curves for the three types of photometric indication have also been derived by various authors. These derivations, although theoretically interesting, are somewhat similar to those outlined in Chapter II and will not be presented in the following discussions. However, some titration curves for each type of photometric indication, calculated using the results of these derivations, will be presented in order to more fully

explain the principles and problems involved in each type of indication. For complete derivations and a more thorough discussion of results, the reader is referred to the literature.

Flaschka (35) has derived equations for both the self-indicating and slope-indicating cases for chelometric titrations in which 1:1 complexes are formed.

The results of the derivation for a self-indicating system show that useful titrations are possible when the product $K_{MY}\ C_M$ is as low as 50. As the product $K_{MY}\ C_M$ decreases, the photometric titration curve deviates more and more from linearity in the vicinity of the end point, and the curve becomes horizontal for small values of $K_{MY}\ C_M$ only after the addition of a large excess of titrant. Figure 7 shows the calculated photometric and logarithmic (pM) titration curves for the value of $K_{MY}\ C_M = 50$. The advantage of a photometric titration as compared to a pM titration is evident from this plot.

The results of the derivation for a slope-indicating system reveal that a metal M can be successfully titrated using an equal concentration of a metal N as a slope indicator when the ratio of conditional constants K_{MY}/K_{NY} is 100 or greater. The shape of the titration curve depends on the ratio K_{MY}/K_{NY}. For a large value of K_{MY}/K_{NY}, the titration curve will show a sharp break at the first end point. If K_{MY}/K_{NY} is small, the titration curve is drawn out in the vicinity of the end point. If this curvature is severe, the location of an end point is difficult or impossible. Figure 8 shows the calculated photometric and logarithmic (pM) titration curves for a solution 1×10^{-2} F in M and N with $K_{MY}/K_{NY} = 100$. Again it can be seen that the application of a photometric titration is

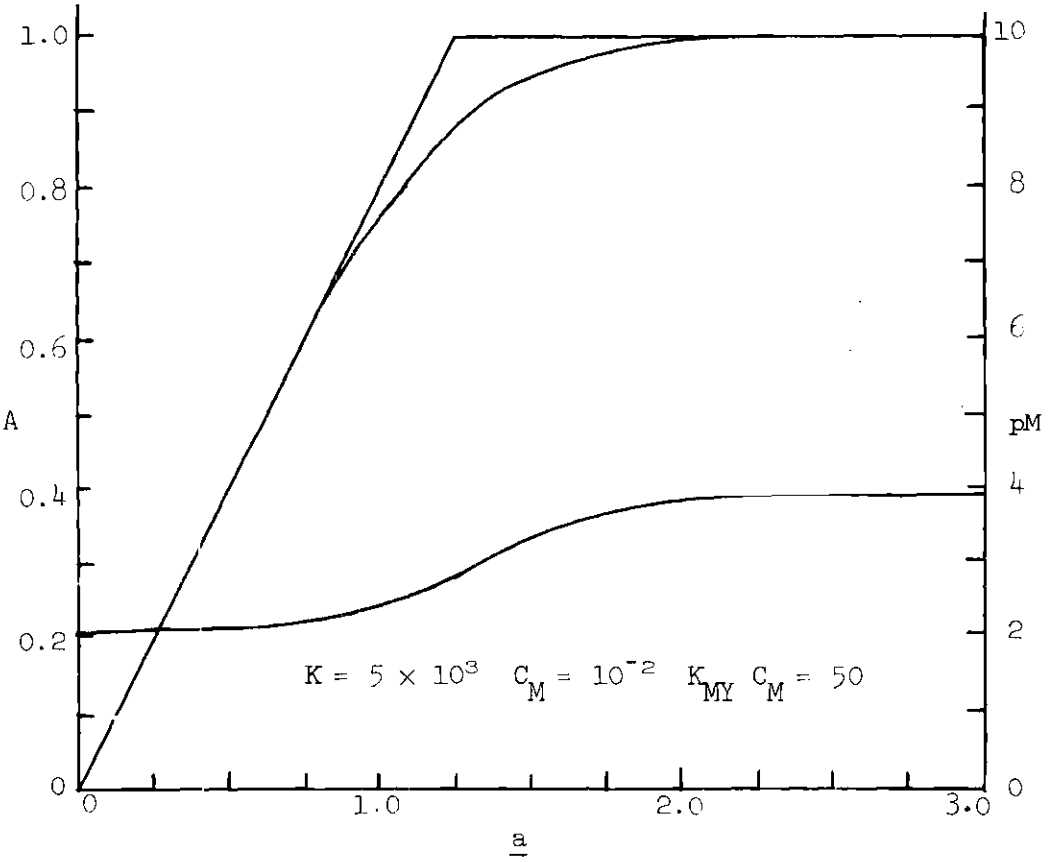

Figure 7. Calculated Photometric and Logarithmic Titration Curves for a Single Metal System

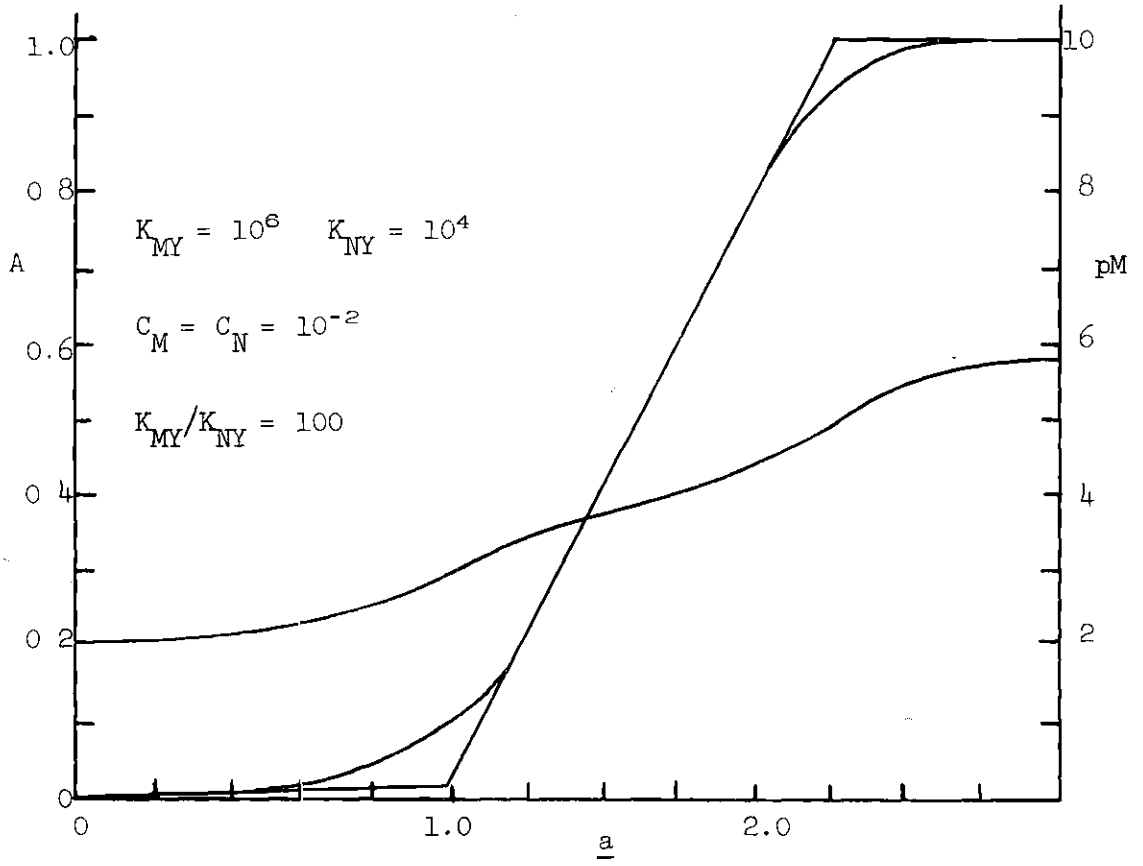

Figure 8. Calculated Photometric and Logarithmic Titration Curves for a Two Metal System

most advantageous in such a case.

Theoretical studies of step-indicating systems have been carried out by a number of workers (36, 37). These studies show that a sharp end point is obtained when K_{MY}/K_{MI} is greater than 10^4, K_I itself is greater than 10^4, the indicator concentration is low, and the metal concentration is high. However, no completely general studies were undertaken. Flaschka and coworkers (38) made a general study of step-indicating systems using computer techniques to minimize labor and to avoid the use of mathematical approximations. Calculations were made for many different numerical values of the parameters K_{MY}, K_{MI}, C_M, and C_I. Figure 9 shows the calculated photometric titration curves for various values of the indicator constant K_{MI} where $K_{MY} = 10^{10}$, $C_M = 10^{-3}\underline{F}$, and $C_I = 10^{-5}\underline{F}$. It can be seen that for this particular case a low value of K_{MI} (i.e., $K_{MI} = 10^3$) causes considerable curvature before the end point and no sharp break is obtained. A high value of K_{MI} (i.e., $K_{MI} = 10^{10}$) on the other hand causes considerable curvature after the end point and again no sharp break is obtained. However, end points can be located for both cases. Titration curves for intermediate values of K_{MI} exhibit more pronounced breaks near the end point. The titration curve for $K_{MI} = 10^7$ is nearly an ideal step-indication curve.

Figure 10 shows the calculated photometric titration curves for various indicator concentrations where $K_{MY} = 10^{10}$, $C_M = 10^{-3}\underline{F}$, and $K_{MI} = 10^5$. These curves show the effect of increasing the indicator concentration on a system which, at low C_I, would give a break at the end point and illustrate a most interesting conclusion drawn from these calculations. It can be seen that as C_I is increased, the portion of the titration curve

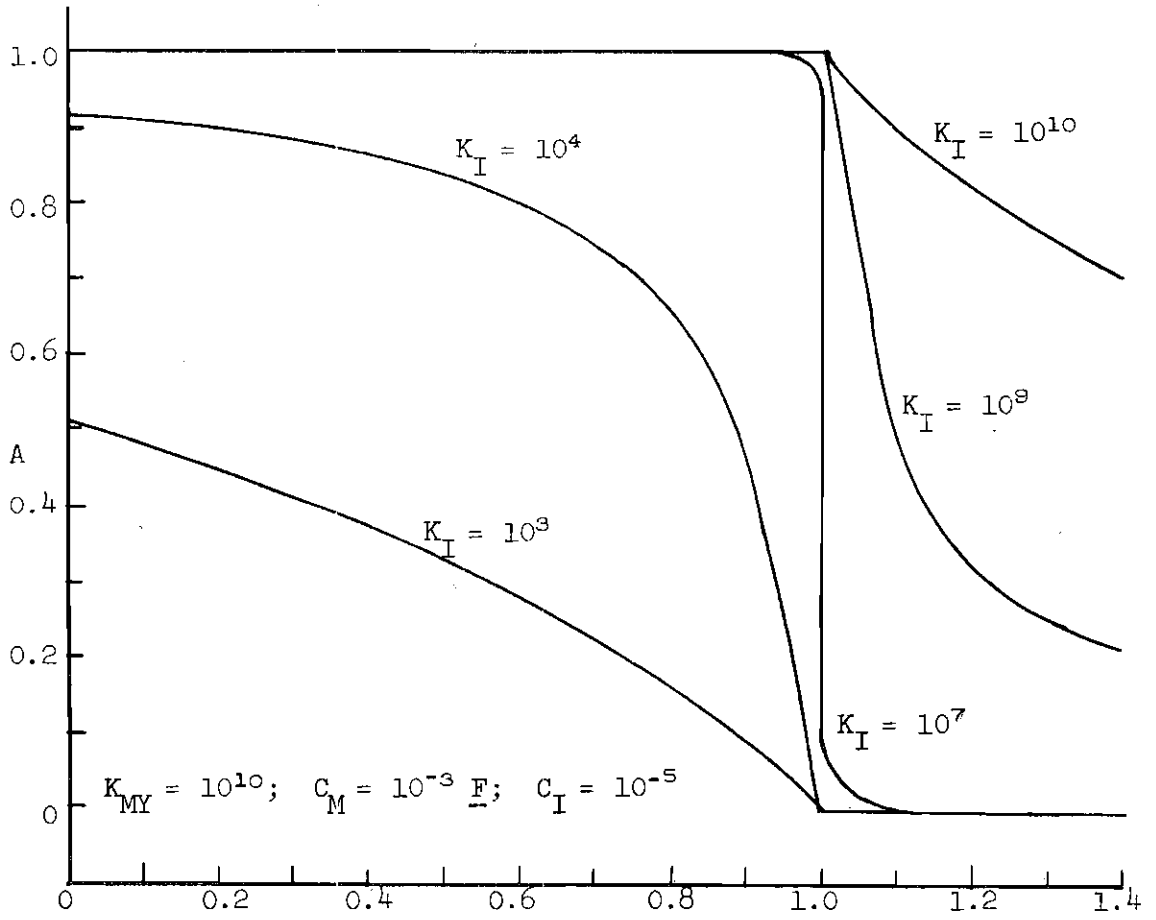

Figure 9. Influence of K_I on a Photometric Titration Curve

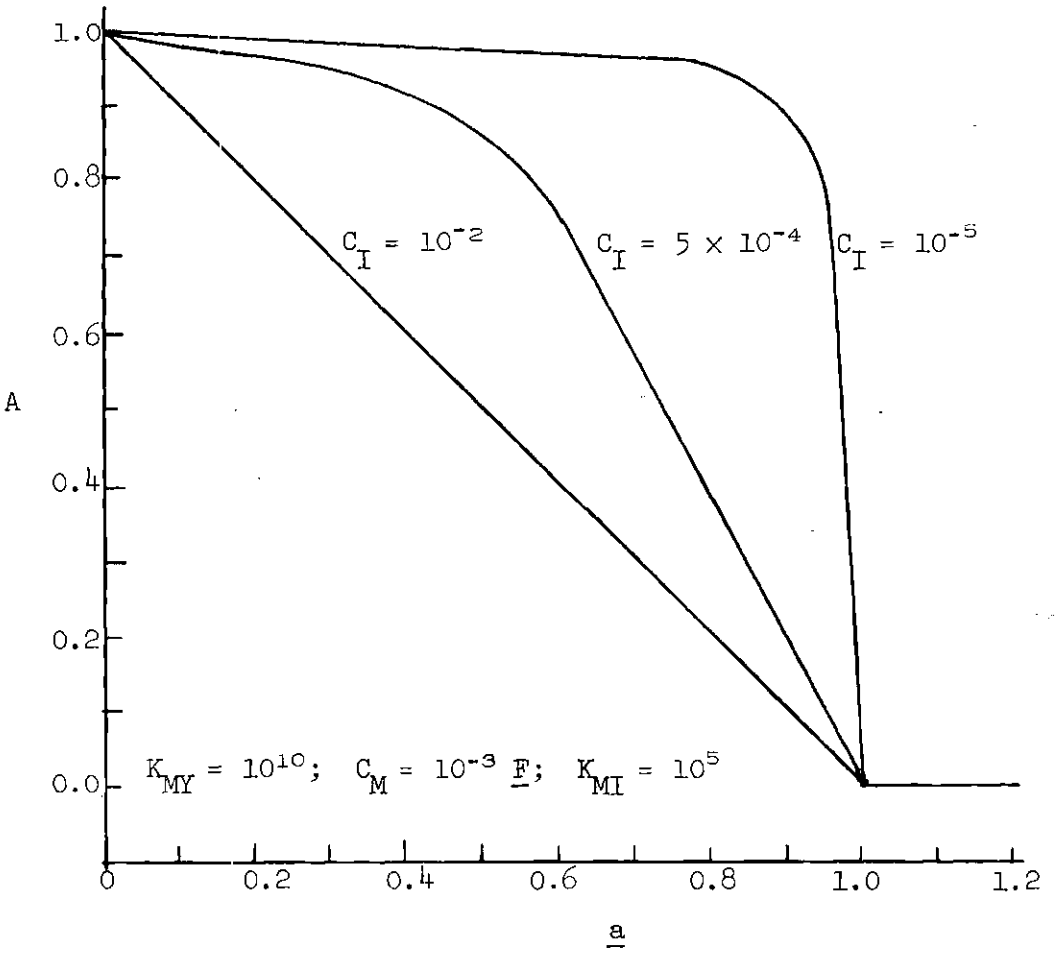

Figure 10. Influence of C_I on a Photometric Titration Curve

before the end point becomes increasingly rounded until, ultimately, a self-indicating system is obtained. In general a self-indicating photometric titration curve is obtained on the addition of an indicator whenever

$$C_I \geq 10\ C_M$$

$$K_{MY} > 10^6$$

$$K_{MI} \leq 10^{-1}\ K_{MY}\ C_M$$

Thus it is possible to create a self-indicating system by the addition of an excess of a metal indicator. Such self indication may be used for the titration of one metal, or to indicate the end point in the titration of another metal (which must complex strongly with the titrant and weakly or not at all with the indicator). Thus, the possibility exists for a consecutive titration of two metals. Three titration methods employing this principle have been reported. In the first method, submicrogram amounts of calcium and magnesium were titrated with EDTA at pH 10 using magnesium-Calmagite as the slope-indicating system (30). The other two methods employed the zinc-Murexide (39) and the zinc-Zincon (40) systems as the slope-indicating systems for the EDTA titration, cadmium at pH 10.

CHAPTER V

EQUIPMENT AND CHEMICALS

Photometric Titrator

The photometric titrators used in this research were designed and built by Flaschka and Sawyer (41), and Flaschka and Butcher (49). With these instruments, titrations are performed with the titration vessel in the open. The design features of the first of these instruments (41) are discussed in Chapter IX.

Titration vessels were constructed from rectangular pieces of plate glass, bonded with epoxy glue. The stirrer was a glass rod with a small propeller at the lower end and was driven by a small six volt motor.

Other Instruments

Spectrophotometers

All spectral curves were made with a Bausch and Lomb Spectronic 505 recording spectrophotometer. Screen calibrations were made with a Cary Model 14 recording spectrophotometer.

pH Meter

All pH measurements were made with a Leeds and Northrup #7664 pH meter. The instrument was standardized with a potassium acid tartrate buffer (saturated solution, 25°C, pH 3.57).

Potentiometer

All potential measurements were made with the Beckman Research Model pH meter.

Glassware

The usual laboratory glassware such as beakers and flasks was used as needed. All volumetric glassware was Class A and was used without additional calibration.

Chemicals

Water

Deionized water was used exclusively.

Disodium (Ethylenedinitrilo)tetraacetic Acid Dihydrate (EDTA)

J. T. Baker Chemical Company "Baker Analysed" disodium EDTA was slurried in several hundred milliliters of water and a few pellets of sodium hydroxide were added to hasten dissolution. The solution was prepared to be approximately 0.1 F (37.2 g/l) and was standardized against a standard zinc solution.

Xylenol Orange

J. T. Baker Chemical Company xylenol orange was used. The indicator solution was prepared by dissolving 0.1 g of the tetrasodium salt in 100 ml of water.

Sulphosalicylic Acid

Baker reagent grade sulphosalicylic acid was used. The indicator solution was prepared by dissolving 1 g of the acid in 10 ml of water.

1-(2-Pyridylazo)-2-naphthol (PAN)

Baker reagent grade PAN was used. A 0.01 F indicator solution was prepared by dissolving 0.622 g of the solid indicator to 250 ml with 95 percent ethanol.

Acids

DuPont concentrated nitric, hydrochloric, sulfuric, and perchloric

acids were used as required.

Bases

DuPont concentrated aqueous ammonia and J. T. Baker "Analysed" sodium hydroxide pellets were used as required.

Zinc Standard Solution

A standard 0.1000 F zinc solution was prepared by dissolving 6.538 grams of Baker "Analysed" zinc metal (99.99 percent pure) in the minimum amount of nitric acid. The solution was then boiled briefly to expel oxides of nitrogen, cooled, and diluted to one liter.

Metal Salt Solutions

J. T. Baker "Analysed" metals and metal salts were used to prepare the desired solutions. In the cases of strongly acidic metal ions, acid was added to reduce hydrolysis.

Iron

An approximately 0.1 F iron solution was prepared by dissolving 40 grams of iron(III) nitrate in one liter of water. This solution was standardized by a photometric titration with a standard EDTA solution at pH 2-3 using sulphosalicylic acid as indicator.

Bismuth

An approximately 0.6 F bismuth solution was prepared by dissolving 290 g of bismuth nitrate in water to which several ml of concentrated nitric acid had been added and diluting to one liter.

Gallium

An approximately 0.01 F gallium solution was prepared by dissolving about 0.7 g of gallium metal in the minimum amount of perchloric acid and diluting to one liter.

Indium

An approximately 0.3 F indium solution was prepared by dissolving 8.6 g of indium metal in the minimum amount of perchloric acid and diluting to 250 ml.

Nickel

A 0.5 F nickel solution was prepared by dissolving 29.35 g of nickel metal (99.9 percent pure) in a minimum amount of 1:1 nitric acid and diluting to one liter.

Cobalt

A 0.100 F cobalt solution was prepared by dissolving 1.473 g of cobalt metal (99.9 percent pure) in a minimum amount of 1:1 nitric acid and diluting to 250 ml.

Ammonium Chloride

Ammonium chloride was used as the solid salt. Reagent grade ammonium chloride was used throughout most of this work; however, U.S.P. grade ammonium chloride proved satisfactory in some cases.

Other Chemicals

All other chemicals were Baker "Analysed" reagents except that Eastman l-ascorbic acid was used.

Standardization Procedure

EDTA Standardization

An aliquot of the standard zinc solution was pipetted into a flask and diluted with water. A few milliliters of an acetate buffer pH 5 were added along with one or two drops of xylenol orange solution. The resulting solution was then titrated with an EDTA solution until the indicator

color changed from red to yellow.

Storage of Solutions

All chelon and indicator solutions, all alkaline solutions, and all dilute (0.001 F or less) metal ion solutions were stored in polyethylene bottles.

CHAPTER VI

THE EDTA TITRATION OF IRON(III) IN THE PRESENCE OF HIGH CONCENTRATIONS OF BISMUTH

Introduction

The direct chelometric titration of bismuth when present as the chloride is usually difficult, because of the formation of the insoluble oxychloride. It is known that high chloride concentrations prevent the formation of the oxychloride, or redissolve it once it has formed, provided that the pH is lower than about 3. It was thought that addition of high concentrations of chloride might offer a possibility for the direct titration of bismuth because, in such a solution, no precipitate would form. However, under these conditions bismuth gave only a faint color or no color at all with several metal indicators tried, and the rate of reaction of bismuth with EDTA was, from all indications, slow. These experimental findings suggested the possibility of using chloride for the "low stability masking" of bismuth.

To test this idea an attempt was made to titrate iron in the presence of bismuth, masking the latter by chloride. The stabilities of the EDTA complexes of iron and bismuth are of nearly the same order. Consequently the metals mutually interfere in titration. Although it is not difficult to titrate bismuth in the presence of iron when the latter is masked by reduction to iron(II) with ascorbic acid (42), the determination of iron in the presence of bismuth was previously possible only by differ-

ence methods. The sum iron + bismuth is titrated in one aliquot, and the bismuth is titrated in a second aliquot, after the iron is masked by reduction. The iron is obtained by difference. This procedure yields good results for iron only if the Bi:Fe ratio is close to or below unity. With bismuth present in increasing excess, the results for iron rapidly become less accurate.

Sulphosalicylic acid was employed as the indicator for the titration of iron at pH 2-3. Preliminary experiments revealed that the color of the iron-sulphosalicylic acid complex is discharged only slowly after the addition of excess EDTA, when the amount of ammonium chloride added is not higher than that required to redissolve the bismuth oxychloride initially formed. But with the solution nearly saturated with ammonium chloride, the color disappears rapidly with a seemingly equivalent amount of EDTA. However, the disappearance of the red color at the end point was only gradual, especially with a large excess of bismuth present. Thus, in this particular case, no visual end point could be obtained and a photometric titration was used.

Apparatus

The phototitrator described in Chapter IX was employed with a heat filter mounted in the light path. An interference filter with the nominal wavelength of 508 mμ was used. All titrations were performed in a glass cell with a 2 cm path length and a 200 ml capacity.

Reagents

The reagents were prepared and standardized as described in Chapter V.

Procedure

An accurately measured amount of the metal ion solution was transferred to the titration cell and enough hot water was added to make the solution volume 75-100 ml. Then 20-30 g of solid ammonium chloride were added in 5 g portions, with vigorous stirring, until no more solid was observed to dissolve readily. The remaining solid was dissolved by adding small amounts of hot water, and the solution volume was then brought to about 150 ml with a saturated ammonium chloride solution. The solution was cooled to room temperature, and the pH was adjusted to between 2 and 3 by dropwise addition of dilute sodium hydroxide, with vigorous stirring to minimize the local precipitation of bismuth salts. The cell was positioned in the phototitrator, which was then adjusted to indicate a transmittance of 85-90 percent. Finally, 4-5 drops of indicator were added and the titration was carried out at 508 mμ in the usual manner, with 0.01-0.1 F EDTA.

Results and Discussion

The results of several titrations of iron(III), alone and in the presence of bismuth and other metals, are presented in Table 1. Using the procedure presented above, solutions with a molar ratio of Bi:Fe of 2,100:1 were titrated, and showed the precision and accuracy to be expected with the apparatus and technique employed. When the ratio was increased to 3,000:1 and slightly above, a tendency towards increasing positive errors was observed. Impurities of iron or other titratable metals in the bismuth salt may be responsible for this trend, but it is more likely that, at this high ratio, some bismuth is also titrated.

Table 1. Representative Results for the EDTA Titration of Iron(III) in the Presence of Bismuth and Some Other Metal Ions

Fe taken, mg	1.14×10^{-1} F EDTA, ml			Metal (M) added	Molar ratio M:Fe
	Calculated	Found	Difference		
5.70	0.89	0.89	0.00	---	---
5.70	0.89	0.88	-0.01	---	---
5.70	0.89	0.89	0.00	Bi	2
5.70	0.89	0.87	-0.02	Bi	2
5.70	0.89	0.88	-0.01	Bi	50
5.70	0.89	0.87	-0.02	Bi	100
5.70	0.89	0.89	0.00	Bi	210
5.70	0.89	0.90	+0.01	Bi	420
	5.70×10^{-2} F EDTA, ml				
2.85	0.89	0.90	+0.01	Bi	1050
	1.14×10^{-2} F EDTA, ml				
1.14	1.79	1.79	0.00	---	---
1.14	1.79	1.79	0.00	Bi	2100
1.14	1.79	1.80	+0.01	Bi	2090
1.14	1.79	1.87	+0.08	Bi	3140
1.14	1.79	1.86	+0.07	Bi	3140

Table 1. Representative Results for the EDTA Titration of Iron(III) in the Presence of Bismuth and Some Other Metal Ions (Concluded)

Fe taken, mg	1.00×10^{-2} F EDTA, ml			Metal (M) added	Molar ratio M:Fe
	Calculated	Found	Difference		
1.23	2.20	2.20	0.00	Bi	1570
1.14	2.05	2.08	+0.03	Bi	1450
1.14	2.05	2.14	+0.09	Al	9
1.14	2.05	2.47	+0.42	Al	9
1.14	2.05	2.04	-0.01	Zn	25
1.14	2.05	2.04	-0.01	Ca	25
1.14	2.05	2.04	-0.01	Pb	25
1.14	2.05	2.05	0.00	Pb	125
1.14	2.05	2.05	0.00	Co	50
1.14	2.05	2.04	-0.01	Co	250
1.14	2.05	2.06	+0.01	Hg(II)	500
1.14	2.05	2.06	+0.01	In	1
1.14	2.05	2.06	+0.01	In	10
1.14	2.05	2.05	0.00	Mn	125

The rate of fading of the color of the iron-sulphosalicylic acid complex upon the addition of an increment of titrant solution decreases considerably for Bi:Fe ratios above 1,000:1 and it becomes necessary to wait four to five minutes for the reaction to go to virtual completion after each addition of titrant. However, because only a few points are required for locating the end point graphically, this delay is not too serious. A reasonable explanation for the delayed reaction may be suggested. As the EDTA is added to the solution containing such a high concentration of bismuth, complex formation first occurs with that metal; then the iron exchanges with the bismuth, and this exchange reaction takes place slowly.

A mole ratio, Bi:Fe, of 3,000:1 is equivalent to a weight ratio of approximately 11,200:1. Thus the situation in the artificial solutions parallels the determination of about 0.01 percent of Fe in a bismuth metal sample of which 12 g were taken. The determinations at this ratio were precise to about four percent relative. At these levels of amounts and ratios, the success of a titrimetric determination is rather unusual. It must, of course, be considered that in an actual analysis less favorable results may be obtained because of the presence of interfering impurities.

For the titration of iron at the high Bi:Fe ratios, it is necessary to obtain the maximum amount of dissolved chloride. In order to incorporate as much ammonium chloride as possible, it is helpful to warm the saturated ammonium chloride solution in contact with excess solid salt, before using it to raise the volume of the solution in the titration cell to 150 milliliters.

Predictions about elements that may interfere with the iron titration may be made cautiously from a comparison of the stability constants and from knowledge of the situation in the absence of extreme chloride concentrations. Because iron(III) is known to form chloro complexes, the effective stability constant of the iron(III)-EDTA complex may be lowered to such an extent that the metals which are of no influence under normal conditions may interfere at high chloride concentrations. Several metals were added in order to see if there was a noticeable effect on the position and quality of the end point. No effects were observed with calcium, magnesium, mercury, indium, lead, manganese, or zinc in solutions containing the ratios of metal:Fe indicated in Table 1. No attempt was made to establish limiting ratios. Cobalt slowed the rate of reaction considerably at a ratio of 250:1. Nickel and copper could only be tolerated in concentrations up to about that of iron(III). As expected, aluminum interfered and high results were obtained, implying that this metal is partially titrated. Zirconium and hafnium were fully titrated under these conditions. Gallium, in contrast to indium, was not completely masked by the chloride and high results for iron were obtained at a ratio Ga:Fe as low as one. Titanium slowed the reaction between iron and EDTA to such an extent that the titration became impracticable, even with equal concentrations of titanium and iron.

The interference studies reported are only exploratory in nature, because the main concern of this investigation was masking of bismuth and the determination of iron. The study of the application of low stability masking with chloride, and of the exclusion of some interfering metals by addition of further masking agents is continued in the next chapter with the investigation of the masking of indium by chloride.

CHAPTER VII

THE CHELOMETRIC TITRATION OF GALLIUM IN THE PRESENCE OF INDIUM AND OTHER METALS; CHLORIDE MASKING

Introduction

The chelometric titration of gallium in the presence of indium is not possible under normal conditions since the stability constants of the respective chelon complexes are of the same order of magnitude. Consequently, the two metals mutually interfere in their titration, and a separation was thus far necessary in order to determine either metal in the presence of the other. This separation procedure is often difficult and time consuming. In the investigation described in Chapter VI, it was found that during the titration of iron(III) in a solution containing high concentrations of chloride ion indium could be tolerated in considerably higher amounts than gallium. This fact indicated that indium under these conditions is masked to a certain extent as the chloro complex towards reaction with the indicator Xylenol Orange as well as towards EDTA. Prevention of the reaction between indium and the indicator has also been reported by Danilova (43). A concentration of only one percent in sodium chloride is required to prevent the formation of the colored indium-Xylenol Orange complex. All these findings strongly indicated the possibility that a "low stability masking" of indium by chloride could be performed in order to avoid interference with the chelometric titration of gallium.

Preliminary experiments showed that the gallium-Xylenol Orange com-

plex is not affected by chloride. Unfortunately, at room temperature this complex does not react rapidly with EDTA as was already reported by Kinnunen (44). In boiling solution, however, the reaction was speeded considerably, and the rate was sufficient to permit a visual end point detection. Several other indicators have been investigated (for a selection of these see Schwarzenbach and Flaschka (10)) but none was found superior to Xylenol Orange.

Reagents

All solutions were prepared and standardized as described in Chapter V. Deionized water was used exclusively.

Procedure for the Titration of Gallium

In a 250 ml beaker, place 25 g of ammonium chloride, add the appropriate amount of sample solution, and dilute with water to a total volume of about 100 ml. Stir until all the ammonium chloride is dissolved and adjust the pH to 1.3-1.4* with 1:1 hydrochloric acid. Place the beaker on a hot plate, insert the stirrer and raise the temperature almost to the boiling point. Add 6-8 drops of the indicator solution and titrate with 0.01 to 0.001 F EDTA to a color change from red to pure yellow. Near the end point, wait 20-30 seconds before the next increment of titrant is added because the indicator reaction is slow.

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*One should be aware of the fact that under the conditions prevailing the value of the figures for the pH is problematic. It would be more appropriate to say "insert the glass and reference electrodes and adjust the solution with 1:1 hydrochloric acid until the pH meter reads 1.3-1.4." For the sake of brevity, the above phrasing is allowed to stand, but should, here as well as at other places in this chapter, be taken with the restriction mentioned.

Results and Discussion

The results of several titrations of gallium alone and in the presence of other metals are presented in Table 2. Using the procedure given, solutions with a molar ratio of In:Ga of up to 300 were titrated and showed the precision and accuracy to be expected with the technique employed. A slight tendency towards positive errors in the results for gallium is observed with high In:Ga ratios particularly when it was necessary to increase the solution volume. The assumption that some indium is cotitrated would be a plausible explanation for this fact, but we are more inclined to believe that titratable impurities in the indium solution and particularly in the ammonium chloride are responsible for these positive errors. The fact that these errors are considerably reduced if ascorbic acid is added supports this assumption. As will be shown later, this reagent prevents iron(III) and copper(II) from being cotitrated.

A concentration of ammonium chloride of 25 g per 100 ml was found to be optimum. At a lower ammonium chloride concentration, the amount of indium which could be tolerated became smaller and at higher concentration low results for gallium were obtained.

The concentration of ammonium chloride required for the effective masking of indium was found to be dependent on the indium concentration rather than the In:Ga ratio. An amount of 25 g of ammonium chloride was found to mask up to about 140 mg of indium per 100 ml of solution. Larger amounts of indium have been masked by increasing the volume of the solution while keeping the ammonium chloride concentration constant.

With increasing amounts of indium present, the rate of the color change at the end point was decreased considerably. However, the color

Table 2. Representative Results for the EDTA Titration of Gallium Alone and in the Presence of Indium

Given mg Ga	1.00×10^{-2} F EDTA, ml found	calc.	diff.	gNH_4Cl per 100 ml	Metal added	Mole Ratio M : Ga
4.28	6.08	6.09	-0.01	--	--	---
4.28	6.09	6.09	0.00	--	--	---
4.28	6.09	6.09	0.00		--	---
4.28	6.08	6.09	-0.01		--	---
6.41	9.13	9.12	+0.01		In	16
3.42	4.88	4.87	+0.01	25	In	30
5.13	7.33	7.30	+0.03		In	40
3.85	5.50	5.48	+0.02		In	54
3.42	4.91	4.87	+0.04		In	60
	5.00×10^{-3} F EDTA, ml					
2.14	6.08	6.09	-0.01		In	48
1.71	4.89	4.87	+0.02		In	60
2.56	7.30	7.30	0.00	25	In	80
2.14	6.09	6.09	0.00		In	96
1.71	4.90	4.87	+0.03		In	120
	1.00×10^{-3} F EDTA, ml					
0.470	6.73	6.69	+0.04		In	220
0.428	6.09	6.09	0.00		In	240
0.385	5.51	5.48	+0.03	25	In	270
0.342	4.87	4.87	0.00		In	300
0.428	6.08	6.09	-0.01		In	300

Table 2. Titration of Gallium in the Presence of Some Other Metal Ions (Concluded)

Given	1.00×10^{-2} F EDTA, ml			Metal	Mole Ratio
mg Ga	found	calc.	diff.	added	Metal:Ga
4.28	6.08	6.09	-0.01	Ag	20
4.28	6.08	6.09	-0.01	Bi	10
4.28	6.08	6.09	-0.01	Ca	20
3.42	4.89	4.87	+0.02	Cd	12
4.28	6.07	6.09	-0.02	Cd	40[a]
3.42	4.89	4.87	+0.02	Co	2
4.28	6.09	6.09	0.00	Cr^{III}	1
4.28	6.07	6.09	-0.02	Cu	20[b]
4.28	6.05	6.09	-0.04	Cu	40[b]
4.28	6.09	6.09	0.00	Hg	20
4.28	6.07	6.09	-0.02	Fe	20[b]
4.28	6.09	6.09	0.00	Fe	40[b]
4.28	6.08	6.09	-0.01	Fe	200[b]
4.28	6.09	6.09	0.00	Mg	20
4.28	6.08	6.09	-0.01	Mn	20
3.42	4.87	4.87	0.00	Ni	2
4.28	6.09	6.09	0.00	Pb	20
4.28	6.08	6.09	-0.01	Tl	20
4.28	6.09	6.09	0.00	Zn	10
4.28	6.07	6.09	-0.02	Zn	40[a]

[a]Potassium iodide added.

[b]Ascorbic acid added.

change was sufficiently rapid with indium concentration of up to 140 mg per 100 ml to allow the titration to be performed easily. It was possible to carry out the titration at considerably higher indium concentrations; however, near the end point it then became necessary to wait several minutes after each addition of titrant. In addition, a slight excess of EDTA had to be added in order to establish the pure yellow color of the free indicator. A plausible explanation of this extreme retardation of the color change is as follows. Slightly before the end point, the solution contains gallium as the Xylenol Orange complex and a rather large amount of indium. Upon the addition of the titrant solution, the EDTA at first complexes with the indium, and the indium-EDTA complex then reacts at a very low rate with the gallium Xylenol Orange complex. In order to find the optimum pH for the titration of gallium, studies were made on the rate at which the red color of the gallium Xylenol Orange disappeared upon the addition of an excess of EDTA. It was found that a pH of 2 or higher the color disappeared so slowly that a titration became impossible. At a pH below 2, the color change was much more rapid; however, when attempts were made to perform the titration at a pH of 1 or below, the end point was less sharp and low results for gallium were obtained. This is probably due to the weakening of the gallium-Xylenol Orange complex. A pH of 1.3-1.4 was found to be optimum. At this pH value, the end point was sharp and the theoretical amount of EDTA was required for the titration of gallium.

Ordinarily, predictions as to possibly interfering ions in a chelometric titration may be made by examining the stability constants of the metals involved. However, in the presence of such high concentrations of ammonium chloride such predictions are to be made with extreme caution.

The evaluation has to be based on the use of effective stability constants, which, for the prevailing conditions, are difficult to calculate, since the influence of chloro complex formation as well as ionic strength effects have to be considered. In many instances the expectations drawn from theoretical considerations and from previous experimental experience were verified when performing gallium determinations in the presence of other metal ions.

No effect was observed with bismuth, calcium, mercury(II), magnesium, manganese, silver, thallium, and lead in solutions containing the metal:gallium ratios indicated in Table 2. No interference was observed with cadmium or zinc at mole ratios Cd(Zn):Ga up to 10; however, at higher ratios the color change at the end point was slowed considerably. The addition of a minimum of 10 g of potassium iodide per 100 ml of solution allowed the titration to be carried out at the normal rate. Iron(III) both blocked the indicator and was cotitrated with the gallium. If the iron(III) was reduced to iron(II) by the addition of ascorbic acid, no interference was observed. Copper(II) interfered but on reduction to copper(I) with ascorbic acid the interference was removed. Nickel and cobalt interfere at molar ratios greater than about 2, due mainly to the intense color produced by these metals in the solution. Sulfate ion was found to cause a considerable decrease in the rate of the color change at the end point and could be tolerated only in small amounts. Zirconium and hafnium were cotitrated. Thorium is also cotitrated. Unfortunately, the masking of thorium by sulfate cannot be applied, because the amount of sulfate necessary for an effective masking is far above the limit tolerable for

the gallium titration as mentioned above. Aluminum interferes even in small amounts, and no possibility of masking it could be found although considerable effort was spent in this direction. A separation is necessary, and fortunately can be performed in a relatively simple fashion as was reported by Brooks and Lloyd (45). Gallium can be extracted as its chloro complex from solutions 7F in hydrochloric acid into isopropyl ether. Aluminum under these conditions is not extracted, but about five percent of any indium present goes into the organic layer. Thus, a combination of the extraction with the titration procedure proposed here offers a convenient possibility to determine gallium in the presence of aluminum and indium and possibly other metals. The extraction may also serve well in cases where gallium is to be determined in the presence of amounts of indium which cannot be masked by chloride during the titration. The extraction achieves an enrichment of the gallium, and a ratio of indium: gallium prevails in the extract which permits successful application of the chloride masking for indium.

Procedure for the Extraction of Gallium

Place the sample in a 150 ml separatory funnel and add 29 ml of concentrated hydrochloric acid to make the solution 7 F when diluted with water to a final volume of about 50 ml. Extract this solution with three 20 ml portions of isopropyl ether. If aluminum is present, wash each ether extract with a 10 ml portion of 7 F hydrochloric acid to remove any aluminum included in the extract and combine the aqueous phase with the original solution before making another extraction. Evaporate the combined ether extract to dryness, redissolve the residue, and treat as in the titration procedure described above.

CHAPTER VIII

THE PHOTOMETRIC DETERMINATION OF TRACES OF COBALT IN NICKEL; PARTIAL MASKING WITH EDTA

Introduction

Several photometric methods for the determination of cobalt in nickel have been proposed (46, 47); however, these methods are somewhat insensitive due to their limitations in sample size. A modification (48) of the direct photometric method for the determination of traces of cobalt using nitroso-R (46) has been reported. This method involves the separation of nickel prior to the photometric determination by the conversion of cobalt to a soluble Co(III)-amine complex and the subsequent precipitation of nickel as its hexamminoperchlorate. This method, although sensitive, requires considerable sample manipulation and may be subject to losses due to coprecipitation phenomena. Thus, it was of interest to investigate a method which would require no preseparation of nickel and would not be limited as to sample size.

Experimental

It has been known for some time that upon the addition of PAN to a slightly acidic, 50 percent ethanol-water solution of cobalt the initial red color of the solution is rapidly converted to green. Treatment of this solution with concentrated hydrochloric acid does not destroy the green color, whereas, treatment with reducing reagents such as ascorbic

acid removes the color slowly. Also, this green color does not form in solutions which have been deaerated by bubbling with nitrogen prior to the addition of PAN. Thus it can be concluded that the red Co(II)-PAN complex initially formed is oxidized by dissolved oxygen in the solution to form a very stable green Co(III)-PAN complex. Further investigation revealed that in the presence of excess PAN this green colored complex is reproducibly formed, and, after extraction of the complex into chloroform and dilution to a known volume, a plot of the absorbance at 625 mμ versus concentration for solutions containing various amounts of cobalt gives a linear calibration curve as is shown in Figure 11.

Since nickel does not react in a similar manner, it was thought that this phenomenon might result in a simple method for the rapid determination of cobalt in the presence of nickel. This method would consist of the treatment of a 50 percent ethanol-water solution of nickel and cobalt with excess PAN, air oxidation of the cobalt-PAN complex, acidification of the solution to destroy the red nickel-PAN complex, extraction of the Co(III)-PAN and excess PAN into chloroform, and the measurement of the absorbance of the resultant solution. However, on subsequent investigation it was found that this procedure was only satisfactory for a rapid determination if the equivalent amount of PAN used was considerably in excess of the sum of the equivalent amounts of nickel and cobalt present in the solution. If an equivalent amount of PAN in excess of that of cobalt, but less than that of nickel was added, incomplete formation of the green Co(III)-PAN was observed. Thus, for a rapid determination, the total amount of sample taken was limited, and the maximum molar ratio Ni:Co which could be handled was about 10:1.

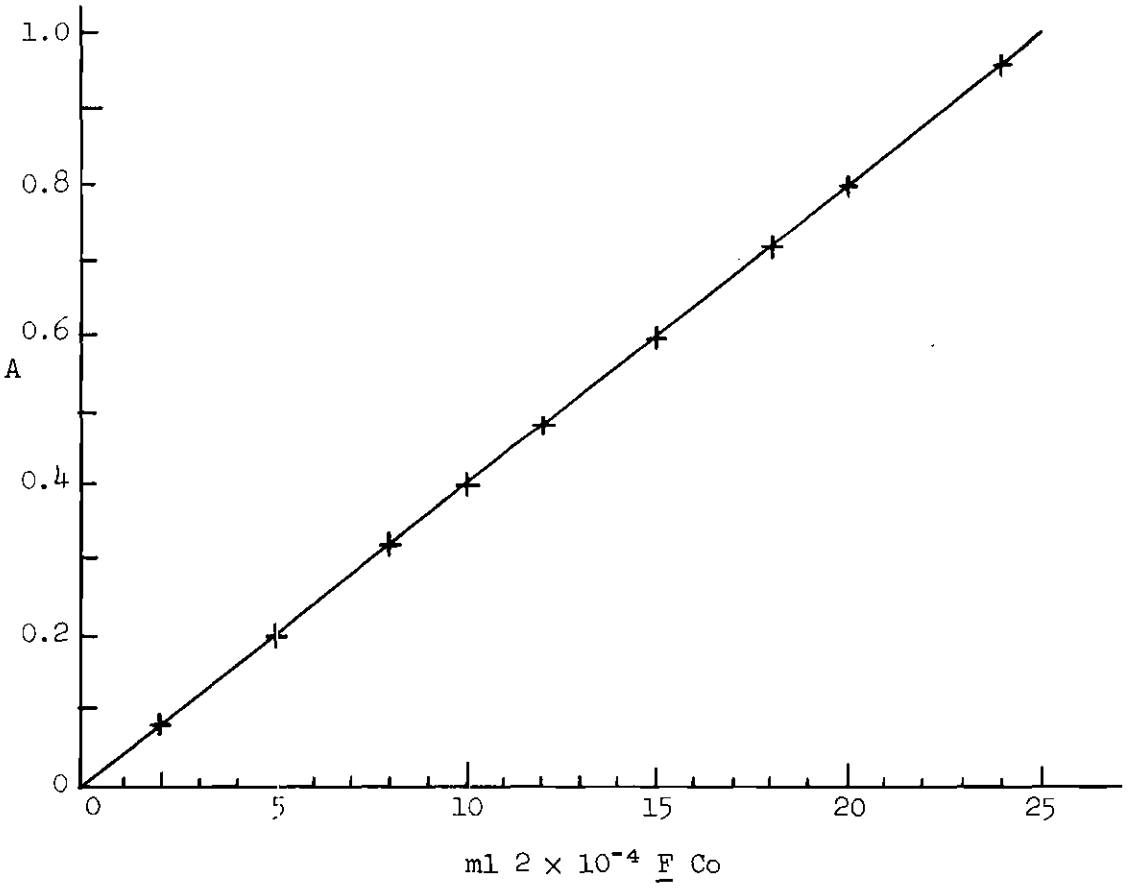

Figure 11. Photometric Calibration Curve for Co(III)-PAN

On subsequent investigation of the rate of formation of the Co(III)-PAN complex in solutions containing various equivalent amounts of nickel in excess of that of the added PAN, it was found that cobalt was completely converted to green PAN complex in about an hour when the molar ratio of Ni:PAN was 5:1 or less, and the solution was bubbled with air or oxygen. For higher ratios, a longer time was required. Although a moderate improvement in the maximum molar ratio Ni:Co (about 200:1) which could be handled was observed, the results obtained were not considered good enough to be used as the basis for an analytical method.

In order to extend the range of the method to higher Ni:Co ratios, several masking studies with conventional masking reagents were undertaken with negative results. EDTA was considered for use as a "partial masking" reagent after it was noted that the stability constant of the nickel-EDTA complex was more than two orders of magnitude greater than that of the corresponding cobalt complex ($\log K_{NiY} = 18.6$, $\log K_{CoY} = 16.3$). This difference in stability is not large enough to permit the titration of nickel with EDTA in the presence of cobalt. However, it was thought to be large enough to allow cobalt to remain essentially uncomplexed after the addition of a fraction of the EDTA equivalent to the amount of nickel present. Under such conditions, nickel would only be "partially masked" as the EDTA complex, since some of the nickel would remain uncomplexed. This "free" or uncomplexed nickel would help to prevent the reaction of cobalt with EDTA.

Studies of the rate of formation of the green Co(III)-PAN complex were carried out for solutions containing nickel and cobalt in various molar ratios and to which was added 50-98 percent of the amount of EDTA equivalent to the nickel. The results obtained were quite similar to those

discussed above. As the molar ratio of the "free nickel" to cobalt increased, the rate of formation of the Co(III)-PAN complex decreased. However, the maximum molar ratio of Ni:Co which could be handled was extended considerably. As a rule it was decided to limit the amount of nickel in excess of the added EDTA such that the ratio "free Ni":Co was 200:1 or lower; thus setting the time required for the complete formation of the Co(III)-PAN complex to about one hour. This "partial masking" technique was found to permit in a relatively simple manner the determination of cobalt at molar ratios Ni:Co as high as 20,000:1.

Reagents

The reagents used were prepared according to the procedure described in Chapter V.

Apparatus

All absorbance measurements were made on the Bausch and Lomb Spectronic 505 recording spectrophotometer. Separatory funnels and other glassware were used as required.

Procedure

Dissolve the nickel sample in a minimum amount of 1:1 nitric acid and dilute to a known volume such that the aliquot portion taken for analysis will contain from 20 to 300 μg of cobalt. Determine the volume of EDTA required by titrating one or two small aliquots of this solution with EDTA in an ammonia-ammonium chloride buffer pH 10 medium using murexide as indicator. Add 90-98 percent of the volume of EDTA calculated from these data to the portion to be analyzed and adjust the volume of the resultant solution with 96 percent ethanol until a 50-60 percent ethanol-water solution results. Adjust the pH of this solution to 2.0-2.5 by the

dropwise addition of 1:1 HCl or concentrated NH_4OH as required. Add 5-10 ml of PAN indicator solution and aerate for a minimum of one hour either by bubbling with air or oxygen, or by shaking frequently in a separatory funnel. After the color has been developed, add a considerable quantity of water and a few milliliters of EDTA in excess. Allow the solution to stand for one to two minutes. Extract several times with 10 ml portions of chloroform until the aqueous phase is free of PAN. Add to the extract 2 ml of concentrated HCl/100 ml final volume and dilute to a known volume with 96 percent ethanol. Measure the absorbance of this solution at 625 mμ against a blank containing the same concentration of HCl and PAN.

Prepare a calibration curve by adding the same amount of PAN indicator solution as is used in the unknown procedure to a series of 50 percent ethanol-water solutions which contain from 1-25 ml of 2×10^{-4} F cobalt solution. Treat each of these solutions as outlined above and plot the absorbance at 625 mμ versus concentration.

Results and Discussion

The results of several photometric determinations of cobalt, alone and in the presence of nickel and some other metals, are presented in Table 3. For solutions containing Ni:Co molar ratios in excess of 2,000:1 a small correction for the trace amounts of cobalt introduced with the stock nickel solution was necessary. A determination of the amount of cobalt in this nickel solution according to the procedure outlined gave a slightly higher result than that given by the manufacturer's analysis. However, the use of either result for the correction of experimental values produced essentially the same correction factor. The observed tendency

Table 3. Representative Results of the Photometric Determination of Cobalt in Nickel and Some Other Metals

ml 2×10^{-4} Co added	ml Found	Diff.	µg Co Added	Ni:Co Molar Ratio
10.00	10.00	0.00	117.9	100†
10.00	10.00	0.00	117.9	100†
10.00	9.90	-0.10	117.9	200†*
10.00	9.95	-0.50	117.9	200†*
10.00	10.00	0.00	117.9	500
8.00	7.97	-0.03	94.30	700
10.00	10.00	0.00	117.9	1,000
5.00	5.00	0.00	58.94	1,000
8.00	8.01	+0.01	94.30	1,000
15.00	14.95	-0.05	176.8	1,000
5.00	4.97	-0.03	58.94	2,000
10.00	10.05	+0.05	117.9	2,000
8.00	8.00	0.00	94.30	2,500
8.00	7.95	-0.05	94.30	3,000
10.00	10.00	0.00	117.9	3,000
5.00	5.00	0.00	58.94	6,000
10.00	10.00	0.00	117.9	6,000
15.00	14.95	-0.05	176.8	6,000
5.00	5.00	0.00	58.94	8,000
10.00	9.95	-0.05	117.9	8,000
10.00	10.00	0.00	117.9	10,000
8.00	8.00	0.00	94.30	12,000
10.00	9.95	-0.05	117.9	15,000*
5.00	4.97	-0.03	58.95	20,000*

Table 3. Representative Results of the Photometric Determination of Cobalt in Nickel and Some Other Metals (Concluded)

ml 2×10^{-4} Co added	ml Found	Diff.	µg Co Added	Ni:Co Molar Ratio
10.00	9.95	-0.05	117.9	20,000*
10.00	9.97	-0.03	117.9	20,000*

†No EDTA added

*Aerated for two hours

towards negative errors is probably due to the incomplete formation or the incomplete recovery of the Co(III)-PAN complex.

The optimum pH range for the formation of the green cobalt complex was found to be pH 2.0-2.5. At a pH higher than 2.5, a lower rate of formation was observed, and at a pH lower than 2.0, erratic results were obtained.

A 50 percent ethanol-water solution is necessary in order to prevent the precipitation of the water insoluble nickel-PAN complex. Incomplete color development was observed for solutions which became turbid due to the precipitation of this complex. In cases where a considerable amount of "free" nickel was present, 60-70 percent ethanol-water solutions were often necessary. Upon the addition of chloroform to solutions containing such a high percentage of ethanol, a single phase is often formed. Thus, in order to insure adequate phase separation, a considerable quantity of water must be added before the extraction can be carried out.

The nickel-PAN complex, if extracted along with the Co(III)-PAN complex, interferes with the photometric determination since it absorbs slightly at 625 mμ. In order to avoid this interference, the nickel-PAN complex is destroyed by the addition of excess EDTA before extraction. Also, HCl is added to the extract in case all of this complex has not been destroyed by EDTA.

The rule that the "free Ni":Co molar ratio should be 200:1 or less cannot be strictly followed for solutions containing large amounts of nickel. For such solutions, a 200:1 ratio corresponds to the addition of 99+ percent of the volume of EDTA required. Positive errors in the results of the pretitrations may lead to the addition of an excess of EDTA in such

a case. Consequently, for solutions having Ni:Co molar ratios in excess of 5,000:1, it was more practical to add 98 percent of the volume of EDTA required. The resultant solutions have "free Ni":Co molar ratios much higher than the prescribed 200:1. The addition of a larger amount of PAN indicator solution and/or aeration for a longer period of time is then necessary to fully develop the green color. With this modification applied, two hours aeration was found to be sufficient for ratios up to 20,000:1.

Copper(II) was expected to interfere with the procedure presented above since it is known to form a very stable PAN complex. It was thought that the formation of this complex would decrease the "free" PAN concentration to such a degree that the reaction between cobalt and PAN would be prevented. It was found that, in the presence of excess PAN, cobalt is completely converted to the green Co(III)-PAN complex in mixtures having Cu:Co molar ratios slightly greater than 1:1. However, at higher molar ratios incomplete formation of the Co(III)-PAN complex results. Although the "partial masking" of copper could possibly be accomplished by the addition of EDTA, this study was concerned only with the determination of cobalt in nickel and no investigations along this line were carried out. If nickel is present such that the Ni:Cu molar ratio is 50:1 or greater, and "partial masking" with EDTA is applied, Cu:Co molar ratios as high as 500:1 can be tolerated. In this case, copper(II) is almost completely in the form of its EDTA complex, and the amount left uncomplexed does not interfere with the reaction between cobalt and PAN. Any Cu(II)-PAN which forms during the course of the reaction is subsequently destroyed by the addition of excess EDTA before the extraction.

Cadmium and zinc did not interfere at molar ratios up to 100:1. However, the rate of formation of the Co(III)-PAN complex seemed to be decreased slightly at molar ratios greater than about 10:1, and a longer aeration period (about two hours) was considered necessary.

Iron(III) forms an extractable red PAN complex which is not destroyed by the addition of excess EDTA or by the addition of HCl to the extract. Thus, iron(III) not only decreases the "free" PAN concentration in the solution preventing the formation of the Co(III)-PAN complex, but also interferes with the photometric determination due to the absorbance of the Fe(III)-PAN complex at 625 mμ. Unexpectedly, this complex is formed even when "partial masking" with EDTA is applied, and a considerable amount of nickel is present. Consequently, iron(III) can only be tolerated for Fe:Co molar ratios of 10:1 or less.

CHAPTER IX

INVESTIGATIONS OF PHOTOTITRATOR LINEARITY

Introduction

During the course of investigations utilizing a modified version of the phototitrator designed by Flaschka and Sawyer (41), a deviation from linearity was observed at wavelengths between 400-500 mμ. A similar deviation was also observed for the original version of the phototitrator in the same wavelength range. A subsequent investigation of the system under consideration indicated that this deviation was not due to some chemical phenomenon and that a linear phototitrator response should be observed. Since the successful application of photometric titrations in this wavelength range is of considerable interest, an investigation to find both the cause of the deviation and the steps which might be taken to produce a linear phototitrator response seemed in order.

First, the properties of an ideal, general purpose phototitrator which would be applicable to any and all nonautomatic photometric titrations should be considered. The characteristics of such an instrument are presented below.

General: A photometric titrator should be rugged, highly stable, relatively inexpensive, and as simple in design and application as possible. Single beam instruments are by reason of their simplicity and lower cost the most useful for this purpose.

Light Source: For a single beam instrument, the light source should

be highly stable with little or no fluctuations in light intensity. Also some means of regulating the light intensity is desirable.

Monochromator: A reasonable degree of monochromacy is necessary and can be achieved satisfactorily by use of a series of interference filters. However, a means of continuously varying the wavelength would be preferred.

Photodetector: The photodetector should be stable, sensitive, and capable of operation over the entire wavelength range of interest. Linear response and absence of fatigue effects are required. The characteristics of the photodetector should not be affected by strong illumination, self-heating, or moderate changes in ambient temperature.

Electrical Circuit: The electrical circuit should be as simple as possible and insensitive to temperature changes and stray magnetic or electrical fields. A provision for scale expansion for use with highly absorbing solutions and for cases where the absorbance changes only slightly during the course of the titration is highly desirable.

Phototitrator Design

The phototitrator designed by Flaschka and Sawyer operates on the following principles: a rather weak, nearly parallel light beam passes through the solution and enters the detector compartment through an interference filter. The light beam is then focused on an extremely small photodetector without being additionally weakened. Due to the optical arrangement, only the light entering within a rather small angle can strike the photodetector, and this angle is considerably less than that subtended by the light housing. Thus, only the extraneous light which has been reflected

or scattered by the titration vessel or the solution need be considered. Further, this extraneous light is white and only the small fraction which is passed by the interference filter strikes the photoreceptor; the amount of such light is negligible.

This instrument has been used for several years and has been generally found to meet the requirements for a phototitrator as presented above. It is extremely insensitive to stray light, stable, inexpensive, and simple in design.

The modified version of this phototitrator was constructed as a part of continuing investigations of phototitrator design. It has the same physical and optical arrangement as the original phototitrator but employs a different type of photodetector.

The photodetector normally employed in the phototitrator is a Texas Instruments IN2175 silicon diffused photoduodiode, which is a very small (12 mm in length, 2 mm in diameter) photoresistive device with a reasonable sensitivity (about 22 $\mu a/mw/cm^2$) throughout the visible region of the spectrum. The modified version of the phototitrator contains a Texas Instruments LS222, which is a photovoltaic device of the same size and approximately the same sensitivity as the IN2175. A new phototitrator circuit was necessitated by the fact that all previous circuits utilized a photoresistive rather than a photovoltaic device. A schematic diagram of the circuit designed for use with the LS222 is presented in Figure 12.

Linearity Investigations

Since the design of both phototitrators excludes interference by

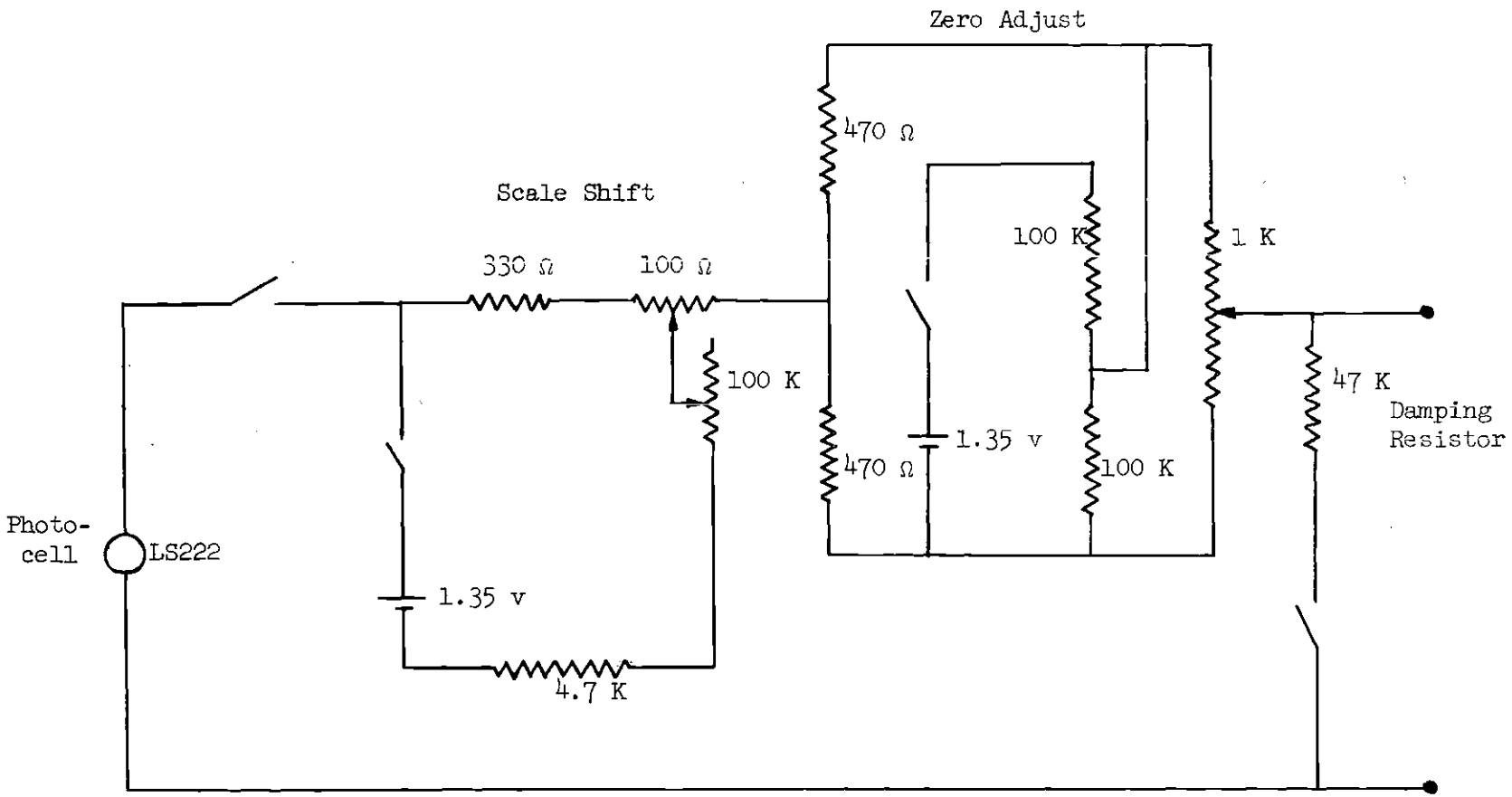

Figure 12. Schematic of the Phototitrator Circuit Employing the LS222

considerable amounts of extraneous light, the deviations from linearity observed between 400-500 mμ must be due to some other aspect of their design. After careful consideration of each design factor, only two possible causes of these deviations could be found. These were:

1. the photodetectors do not give a linear response between 400-500 mμ, and

2. light of some wavelength other than the nominal wavelength of the interference filter is being passed.

Both photititrators were tested for linearity of response by decreasing the radiant power of their light beams with screens. The six screens available were calibrated by measuring their absorbances with a Cary Model 14 spectrophotometer. Then their transmittance (and thus their absorbance) was measured in each photititrator. For each screen, the absorbance measured in both photititrators was found to be higher than that measured in the Cary. If, however, the absorbance of each screen as determined in the Cary was plotted versus the absorbance found with the photititrators, two straight lines with slopes less than one were obtained; these plots are presented in Figure 13. The straight line obtained for the photititrator employing the LS222 corresponds almost exactly to that obtained for the other employing the IN2175. Flaschka and Butcher (49) have explained the phenomena producing the difference in slope of these lines and have shown that such linear plots imply linear photodetector response.

With the stability of both photodetectors assured and their linearity of response strongly implied, it was then necessary to determine whether the interference filters being used were passing light of a

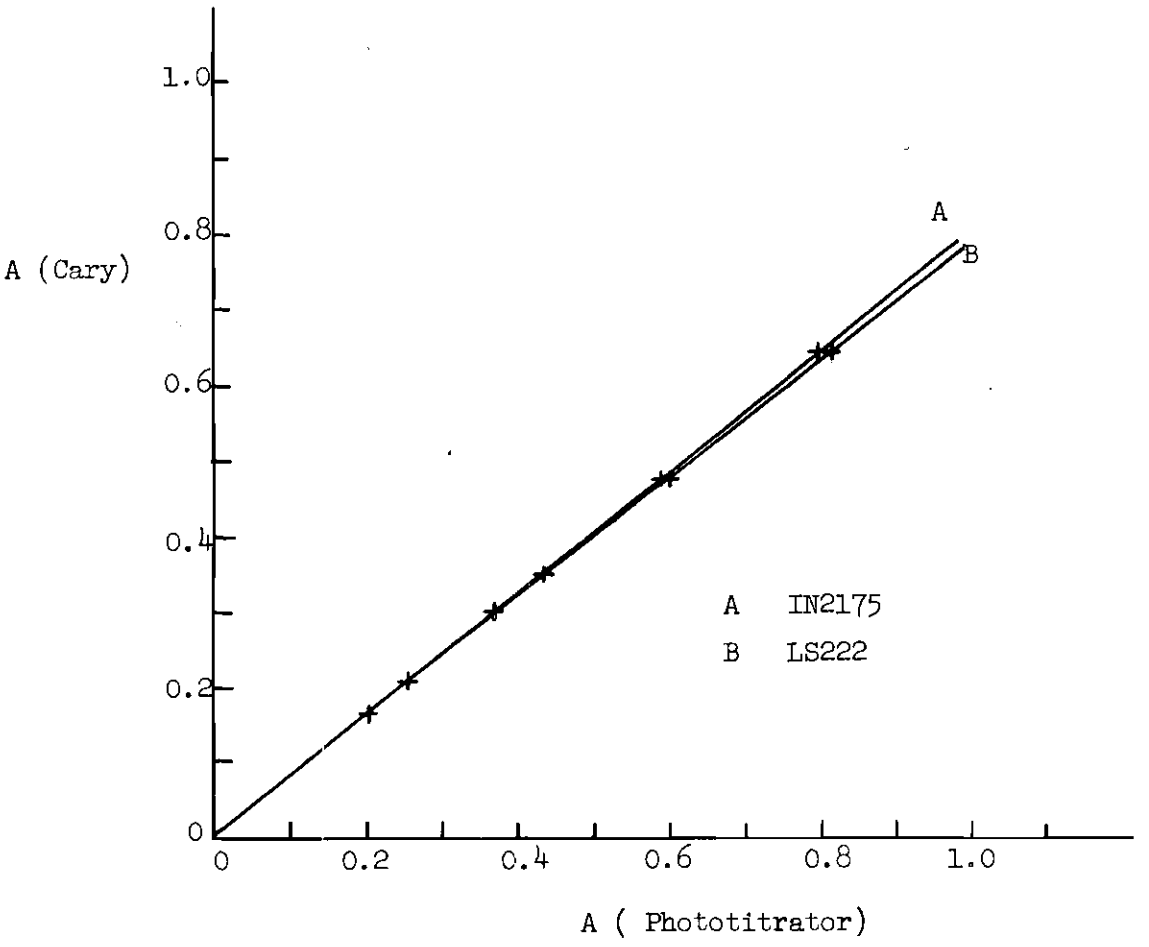

Figure 13. Measured Screen Absorbance for Both Phototitrators

wavelength other than their nominal wavelength.

Infrared light was considered the most likely cause of any deviations from linearity due to nonmonochromacy of the light striking the photodetector. This conclusion was reached because both the IN2175 and the LS222 are much more sensitive in the infrared than in the visible and ultraviolet regions of the spectrum. Also, transmittance curves of the interference filters being used showed no light of any wavelength other than that expected being passed in the visible and near ultraviolet.

In order to test this theory, experiments were performed in which successive increments of methyl orange solution were added to an ammonium acetate buffered solution in a titration vessel. The absorbance of this solution in the phototitrator at 456 mμ was followed. Buffering was necessary in order to prevent equilibrium effects from producing a curvature in addition to that caused by nonmonochromacy. An infrared filter and a wide band interference filter were employed in addition to the primary interference filter in order to attenuate infrared radiation. The curves obtained with and without these filters in the light beam are shown in Figure 14. The #4600 Corning IR blocking filter (Curve B) does not cut off radiation completely below about one micron. Thus, the curvature exhibited when this filter was used was not unexpected. However, when a Baird Atomic wide band interference filter which blocks IR radiation completely and has a half band width of approximately 60 mμ was used, the curve obtained was linear as long as the absorbance of the solution was 1.0 or less (Curve C).

The results of the above experiments prove conclusively that nonmonochromacy due to incomplete blocking of IR radiation is the cause of

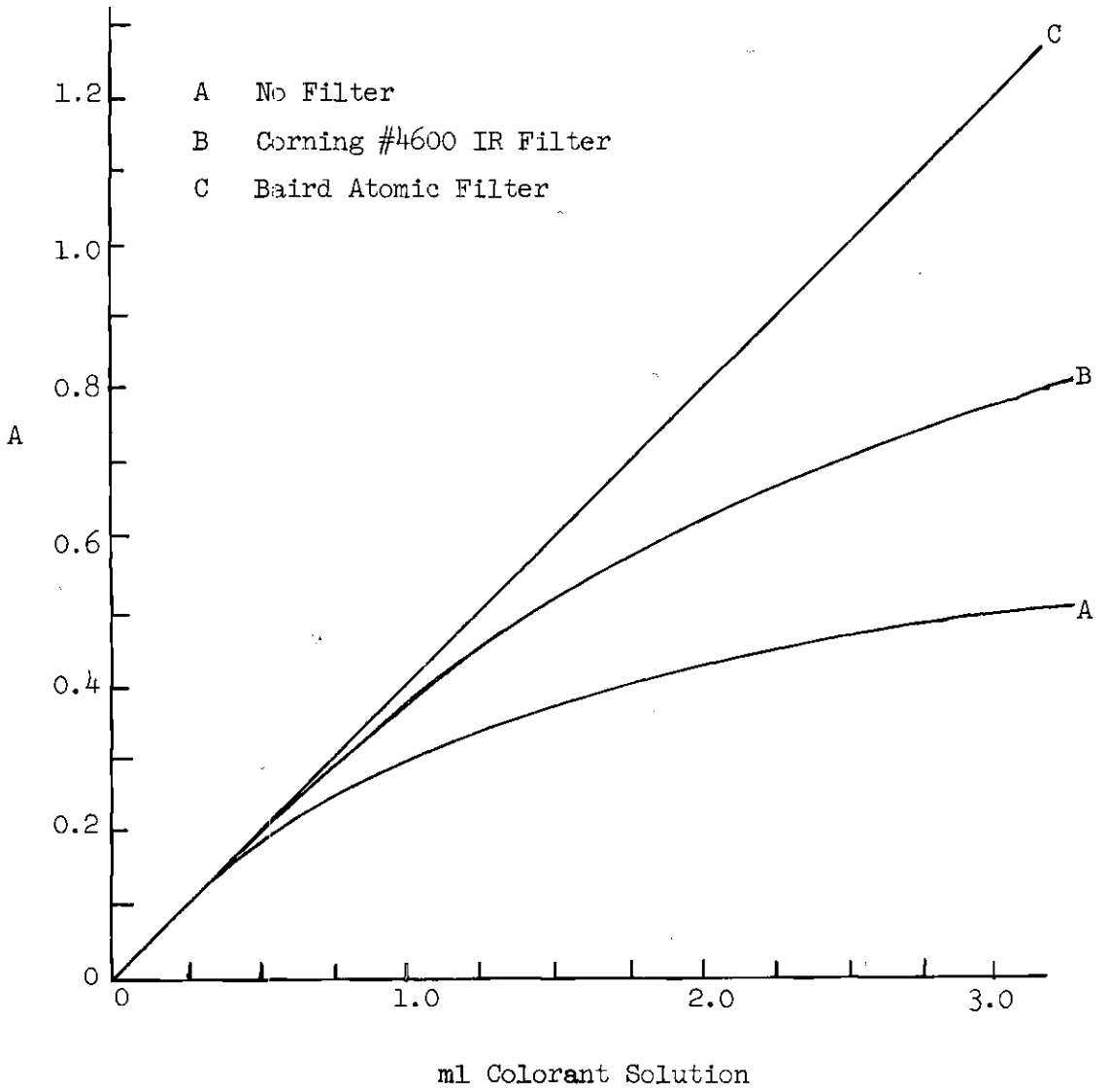

Figure 14. Effect of IR Blocking Filters

deviations from linearity at short wavelengths, and, in order to utilize the short wavelengths for photometric titrations, an interference filter which completely blocks in the IR region, or a combination of an interference filter and a good IR blocking filter must be employed.

CHAPTER X

COMPARISON OF PHOTOMETRIC AND LOGARITHMIC TITRATION CURVES

Introduction

In Chapter IV the results of the derivation of an equation for the calculation of self indicating photometric titration curves were presented. These results show that for a self indicating system a titration is still feasible when the product $K_{MY}^{cond}\ C_M$ is as low as 50. On the other hand, this product must be greater than 10^4 in order to perform a useful logarithmic (pM) titration. Thus, it is apparent that photometric titrations should be of great value for systems where the product $K_{MY}^{cond}\ C_M$ is less than 10^4. However, under experimental conditions, side reactions of the metal ion or chelon, or unaccounted for solution conditions may produce titration curves which do not correspond to those calculated using known stability data. Therefore, it seemed desirable to study one or more systems for which linear and logarithmic titration curves can be obtained simultaneously and to compare these two types of curves with respect to the feasibility of each titration under various solution conditions. In addition, if the value of the product $K_{MY}^{cond}\ C_M$ can be calculated for the experimental system, a meaningful comparison of this value with that obtained by matching experimental and calculated titration curves may be made.

Experimental

In order to obtain titration curves for different values of the product $K_{MY}^{cond} C_{M'}$ two approaches may be taken. Either the concentration of the metal ion or the conditional stability constant of the complex can be varied. Decreasing the concentration of the metal ion to any significant degree produces many experimental difficulties. Thus, it is much more practical to vary the conditional stability constant of the complex. Fortunately, this can be easily accomplished for EDTA titrations by adjusting the pH of the solution appropriately. The conditional stability constant of the complex can then be calculated by the use of the appropriate α factor.

It was necessary to find a metal ion whose titration could be followed by both photometric and logarithmic methods. On examination of the periodic table, only copper(II) seemed likely to meet these requirements. The photometric titration of copper(II) with EDTA can be easily accomplished by following the formation of the blue copper(II)-EDTA complex at 700 mμ. However, finding a suitable logarithmic titration method proved much more difficult. A direct potentiometric titration of copper(II) with EDTA using a platinum indicator electrode and a saturated calomel reference electrode does not yield usable results. The potential measured after the addition of each increment of titrant is subject to rapid and unpredictable fluctuation. This may be explained in the following manner. The potential actually measured is that due to the couple between copper(II) and the small amount of copper(I) present in equilibrium. Apparently the equilibrium concentration of copper(I) varies rapidly when oxygen is introduced as the solution is stirred. Consequently, as long as this situa-

tion exists, no direct potentiometric titration can be performed. Fortunately, a potentiometric titration of copper(II) with EDTA is feasible by stabilizing the copper(I) as its thiocyanate complex (50). The addition of thiocyanate reduces fluctuations of the potential to such a degree that well defined titration curves result.

In order to obtain comparable photometric and potentiometric titration curves, it was decided to perform simultaneous measurements of absorbance and potential. Thus, data for any pair of curves are gathered under exactly the same solution conditions. However, there may be some slight variation between different pairs of curves due to unavoidable differences in the manner in which each solution is prepared.

Procedure

Exactly 200 ml of a 1×10^{-3} F copper solution containing 1 ml of a one percent thiocyanate solution was adjusted to the desired pH and titrated with 0.100 F EDTA. The absorbance of the solution was followed using the semi-immersion phototitrator designed by Flaschka and Butcher (49) adjusted to a path length of four cm. The potential was followed using a Beckman Research Model pH meter.

Results and Discussion

Experimental curves obtained for the titration of 1×10^{-3} F copper(II) solutions at several pH values are presented in Figure 15. As expected, the slopes of the potentiometric titration curves at the end point become smaller as the pH of the solution is decreased. At pH 1.5, the potentiometric titration curve has degenerated to such a degree that no precise determination of the end point can be made, and at pH 1.0, an

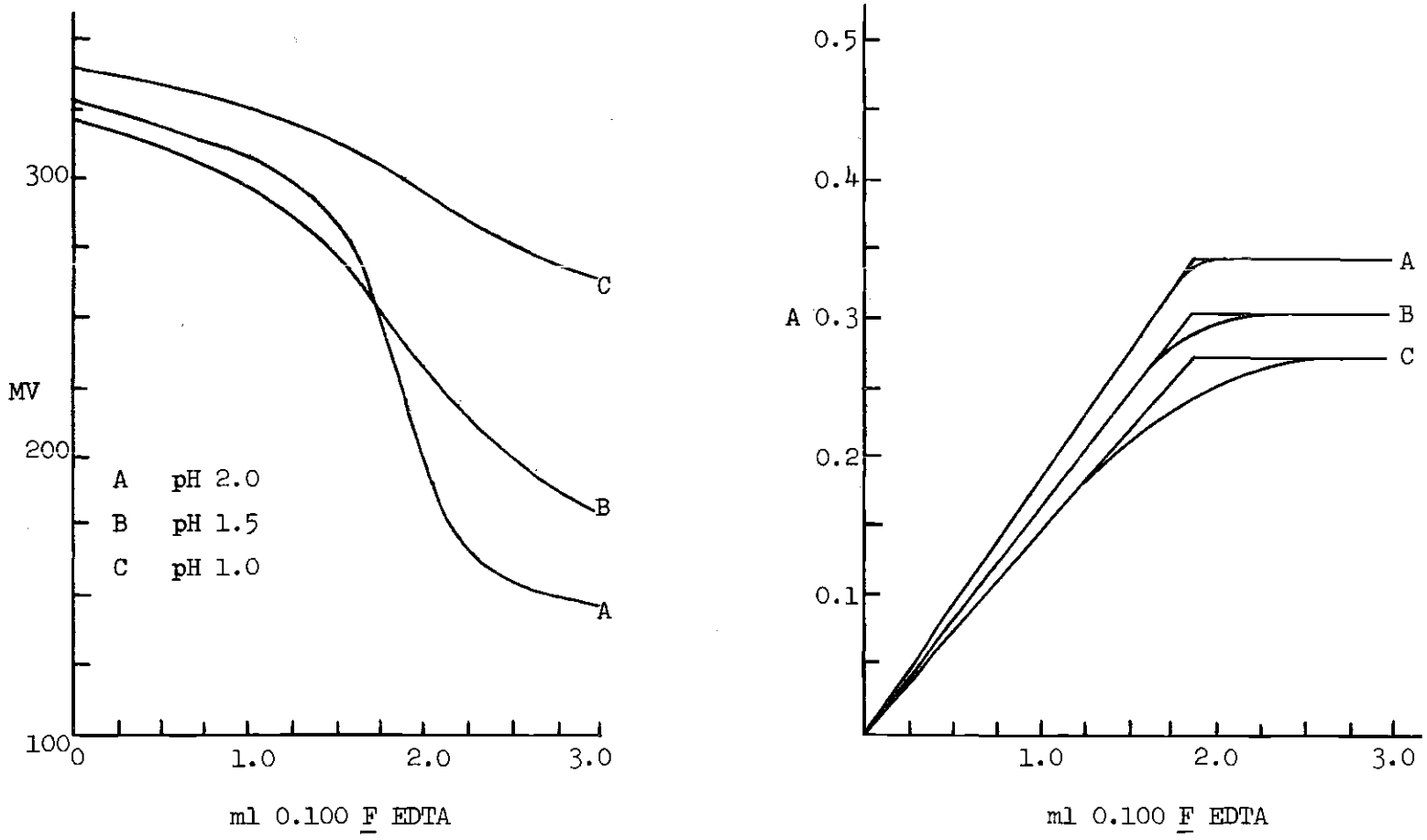

Figure 15. Photometric and Potentiometric Titration Curves

end point cannot be found at all. On the other hand, the photometric titration curves obtained under exactly the same conditions give a clearly defined end point even at pH 1.0. These results confirm the conclusions made on the basis of theoretical calculations as to the usefulness of photometric titrations for such limiting conditions.

The simplest and most direct procedure for determining the value of $K_{CuY}^{cond} C_{Cu}$ for each experimental titration curve is to superimpose a calculated titration curve for which the value of this product is known. However, this procedure cannot be applied with the experimental curves in the form shown in Figure 15, since calculated curves are normally presented in an entirely different form. Calculated logarithmic titration curves are a plot of pM versus the fraction of the metal titrated (a) rather than a plot of potential versus volume. Calculated photometric titration curves, in addition to being a plot of absorbance versus a, are normalized such that the maximum absorbance (i.e., the absorbance considerably past the end point) is unity. Fortunately, it is a relatively easy task to convert the data for both types of experimental titration curves such that a valid comparison can be made. Volume data can be presented as the fraction of the metal titrated (a) by division of the volume at each point on the titration curve by the calculated end point volume. Absorbance data can be normalized by division of the absorbance at each point on the titration curve by the maximum absorbance. After subtracting the 0.242 v due to the saturated calomel electrode from the measured cell voltage, potential data are obtained that can be adjusted to a pM type scale by division by 0.0591.

The "pM" titration curves obtained after such conversions do not

correspond exactly to those calculated, since they are shifted in a negative direction on the pM scale. However, this shift is no hindrance to a comparison of the shape of the curves. Either a visual superimposition can be made, or the shift may be obviated by application of an additive correction such that the initial point on the converted curve corresponds to that for $\underline{a} = 0$ on the calculated curve. Figure 16 shows the experimental titration curves after conversion in the manner discussed above.

Although no exact match of experimental and calculated titration curves could be made, it was possible to make a comparison on an approximate basis. The values of $K_{CuY}^{cond} C_{Cu}$ found at pH 2.0, 1.5, and 1.0, respectively, were approximately 5,000, 500, and 20.

On the other hand, values of the product $K_{CuY}^{cond} C_{Cu}$ calculated using known solution conditions differ greatly from those found by superimposition. The value of this product for each pair of curves was determined using the known copper concentration of 1×10^{-3} $\underline{F}$ and the conditional stability constant for the copper-EDTA complex calculated utilizing equation (11) of Chapter I. At pH 2.0, 1.5, and 1.0, respectively, the calculated values were 130, 2, and 0.03. On the basis of these values alone, titration curves such as those obtained experimentally would not be predicted.

Obviously, some important factor which has a large influence on the conditional stability constant of the copper-EDTA complex has not been taken into account in these calculations. The simplest explanation of the difference of these products is that the tabulated value of the copper-EDTA stability constant is in error. However, this value was experimentally determined in a very rigorous manner, and an error of the magnitude neces-

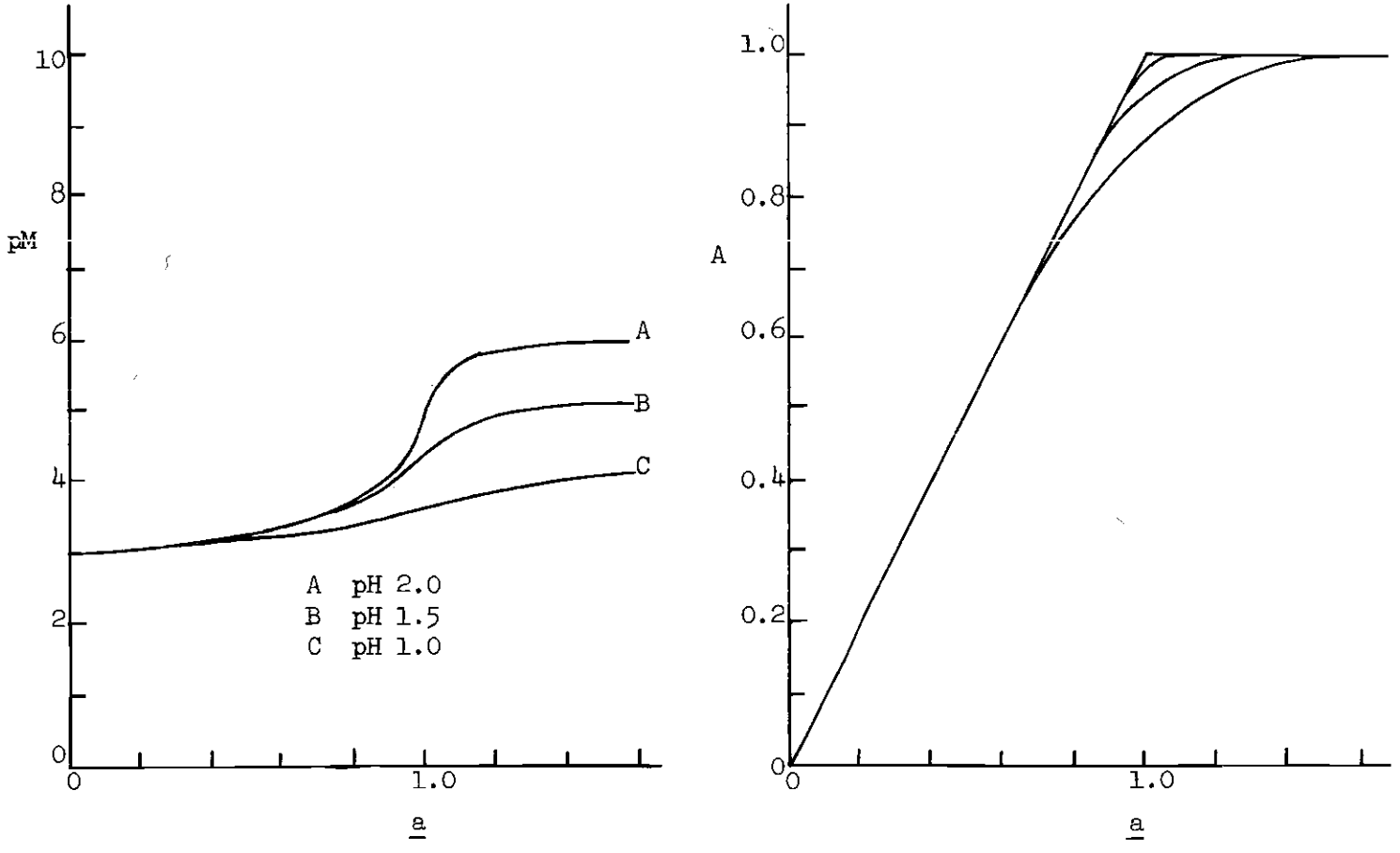

Figure 16. Converted Photometric and Potentiometric Titration Curves

sary to produce such a difference is extremely unlikely. The observed difference in experimental and calculated values of the product could be due to ionic strength effects. As was mentioned in Chapter I, the value of the stability constant of a metal-EDTA complex depends to some extent on ionic strength. The tabulated value of this constant, and the values of the acid dissociation constants for EDTA, which are used to calculate the α factor, are generally determined at a specified ionic strength (usually 0.1). Consequently, these values cannot be strictly applied for calculations at any other ionic strength without introducing an error into the result. The actual values of the copper-EDTA stability constant and the EDTA acid dissociation constants under titration conditions cannot be predicted if no attempt is made to control the ionic strength. Since this was the case for the experimental titration curves, some error in calculated values of the conditional stability constant was expected. Another possible explanation of the observed difference is that mixed complexes of the type $Cu(HY)$, $Cu(H_2Y)$, ..., are formed in solution at such extreme conditions of pH. The effects of the formation of these complexes is not taken into account in the calculations discussed above. The stability constants of such mixed complexes would be considerably larger than those calculated on the basis of equilibrium considerations alone, and much better logarithmic titration curves than expected would result.

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